

Celebrating the

work of

Jacob Israelachvili



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International
Workshop
Cancún, México
May 7-12, 2006



*Bridging
Nanoscale
Forces and
Interfacial
Phenomena to
the Macroscopic
World*

Hotel Presidente Intercontinental
Cancún Center: Conventions and Exhibitions

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***Bridging Nanoscale Forces and
Interfacial Phenomena to the
Macroscopic World***



The organizers for this International Workshop are delighted to invite you to celebrate the work of Professor Jacob Israelachvili

May 7-12, 2006

BLVD KUKULKAN, QUINTANA ROO
CANCUN, 77500
MEXICO

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Topics of the Workshop Include:



Session 1

Nanoscale Forces and Interfacial Phenomena in Soft Materials.

Chair: Professor Tonya Kuhl
co-Chair: Professor Matthew Tirrell



Session 4

Intermolecular Forces between Biomolecules and Their Role in Interfacial Phenomena of Biological Systems.

Chair: Professor Joyce Wong
co-Chair: Professor Deborah Leckband



Session 2

Frontiers in Intermolecular Forces and Interfacial Phenomena.

Chair: Professor Jacob Israelachvili
co-Chair: Professor Philip Pincus



Session 5

Adhesion and Tribological Properties of Films and their Impact in Macroscopic Performance.

Chair: Professor Suzanne Giasson
co-Chair: Professor Octavio Manero Brito



Session 3

Distances and Time Regimes of Intermolecular Forces and their Impact in Materials Behavior.

Chair: Professor Norma Alcantar
co-Chair: Professor Tomas Viveros



Session 6

Intermolecular Forces and Interfacial Phenomena Affecting Structure and Properties of Thin Liquid Films.

Chair: Professor Roger Horn
co-Chair: Professor Dan Schwartz



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Bridging Nanoscale Forces and Interfacial Phenomena to the Macroscopic World

Celebrating the work of Jacob N. Israelachvili

Professor Israelachvili's work has focused on understanding intermolecular and surface forces in complex fluid systems, including colloidal and biological systems. Within this general topic, Professor Israelachvili's research contributions have had a profound effect on our understanding of the basic underlying forces that control the physics of an enormous class of colloid-based and biological materials, and he truly stands out as a modern day giant of the field. In this way, his contributions to the scientific underpinnings of understanding adhesion phenomena have been enormous.

In 1976, Israelachvili and Adams published a landmark paper describing the design of an apparatus in which two solid surfaces could be brought in a controlled way to within a few angstroms of one another in order to measure precise force vs. distance relationships between the solid surfaces. This followed earlier work in the Cavendish laboratory in Cambridge where Tabor's group – including Jacob Israelachvili as a PhD student – developed the idea of measuring forces between crossed mica cylinders. The major advance that Israelachvili and Adams made in Canberra was to build a system that allows force measurements to be conducted in liquids. There are several features of this invention that persist in their power and novelty 30 years later. This surface forces apparatus (SFA) is the only method that can make measurements between two macroscopic surfaces on which controlled surface chemistries can be constructed, in contrast to atomic force microscopy which uses small, generally uncharacterized, probes. The SFA is also the only method that can measure absolute distances since the contact position can be accurately and uniquely determined. There are major classes of problems in intersurface, colloidal, biological and frictional interaction that can only be studied effectively with the SFA. For example, structural or lubrication forces in liquids confined between two solid surfaces are entirely different from those between a probe and a surface. The point is not that SFA is superior to any other method but rather that it is original and uniquely capable of certain deep insights. Only SFA measurements are sufficiently well-defined to be compared quantitatively with theory.

Israelachvili and coworkers have demonstrated the unique and quantitative capabilities of the SFA in a series of papers in the 1980's. His work on structural forces in organic solvents and water is an excellent example. The existence of oscillatory forces had been predicted by theory before they were first observed by Israelachvili and his team. After his careful quantitative measurements, not only were they readily analyzed but compared in detail with theory and computation. A more recent example has been his recent work on the connection between friction and adhesion hysteresis. Again, he has used a powerful, novel tool to produce data that show convincingly that, for viscoelastic polymers, there is a quantitative relationship between adhesion hysteresis, measured by comparing adhesion in separating and joining modes, and frictional forces.

The capability of the apparatus to support a range of interesting surface chemistries was shown by Israelachvili's long series of investigations of supported membranes. He was the first to measure physical forces of membrane fusion and between surface-tethered biological ligand-receptor interactions.

Professor Israelachvili's use of his SFA allowed for the first direct test of existing theories of interaction forces (as in the case of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of the repulsive electrostatic and attractive van der Waals forces between particle surfaces in aqueous solutions). It has also allowed for the establishment of the limits of applicability of some fundamental interactions (as in the case of tests of the limits of applicability of the Kelvin and Laplace Equations of capillary condensation). Finally, as mentioned above, the SFA was used by Professor Israelachvili and his coworkers to discover completely new types of interactions (such as oscillatory solvation forces or the long-range hydrophobic interaction). In the hands of Professor Israelachvili and his colleagues, and later of other groups trained by him or inspired by his work, these SFA's have been used to investigate interactions between surfaces, molecules, polymers and biological structures, and to shed light on the microscopic mechanisms underlying them. The SFA is now used in many university and industrial research laboratories where it has become a standard tool for measuring adhesion, friction, long-range colloidal interactions and many other surface phenomena.

It is also worth mentioning that Professor Israelachvili is the author of a textbook entitled "Intermolecular and Surface Forces" (Academic Press, 1985, 1991) that has become a classic of modern understanding of such forces, and a 'bible' for the community of surface, colloid and complex fluid scientists. It is widely used as a graduate textbook and in university and industrial research laboratories.

Professor Israelachvili has become the leading figure in the area of intermolecular and surface forces, and enjoys wide recognition among physicists, chemists, engineers and biologists. His studies and discoveries using the SFA have revolutionized our conceptual thinking about many aspects of the liquid state and of surface and interfacial forces and dynamics.

It is our pleasure to bring the SFA scientific community together and organize this workshop in his honor.

Sincerely,

SFAC2006 Organizing Committee

CONFERENCE PROGRAM

Saturday, May 6

12:00 pm –	5:00 pm	<i>Arrival and Registration</i>
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Sunday, May 7

7:30 am –	6:00 pm	<i>Chichen Itza Trip</i>
12:00 pm –	5:00 pm	<i>Arrival and Registration</i>
7:00 pm		<i>Welcome Reception</i>

Monday Morning Session, May 8

8:55 am – 12:15 pm

Nanoscale Forces and Interfacial Phenomena in Soft Materials

Chair: Professor Tonya Kuhl; co-Chair: Professor Matthew Tirrell

7:30 am		<i>Breakfast</i>
8:55 am		<i>Introduction</i>
9:00 am		Hard and Soft Nano-Junctions. Uzi Landman
9:25 am		Structural Forces at Aqueous Interfaces. Manfred Heuberger
9:50 am		Selective Coalescence of Bubbles in Simple Electrolytes. Stjepan Marcelja
10:15 am –	10:30 am	<i>Coffee Break</i>
10:30 am		Surfactant Interactions with Polyelectrolytes: Microscopic Binding and Macroscopic Gel Particles. Eric Kaler
10:55 am		Direct Measurement of Adhesion between Identical Polyelectrolyte Brush Layers in the Presence of Multivalent Counterions. Matthew Tirrell
11:20 am		Behavior of End-Grafted Charged Polymers. Suzanne Giasson
11:45 am		<i>Panel Discussion</i>
12:10 pm –	12:15 pm	<i>Final Remarks and Session Closing</i>
12:30 pm		<i>Lunch Break</i>
12:30 pm –	5:00 pm	<i>Jungle Tour (Lunch box will be provided to participants)</i>
5:00 pm		<i>Dinner</i>

Monday Evening Session, May 8

6:25 pm – 9:00 pm

Frontiers in Intermolecular Forces and Interfacial Phenomena (Part I)

Chair: Professor Jacob Israelachvili; co-Chair: Professor Philip Pincus

6:55 pm		<i>Introduction</i>
7:00 pm		Extending the Range and Scope of Surface Force Measuring Techniques. Jacob Israelachvili
7:25 pm		Shedding Light on the Dark Side of Surface Forces. William Ducker
7:50 pm		Using Intermolecular Forces and Interfacial Phenomena to Help Humanity. Norma Alcantar
8:15 pm		A Three Component Force Transducer for Atomic Force Microscopy. Kai Kristiansen
8:40 pm		<i>Panel Discussion</i>
9:10 pm –	9:15 pm	<i>Final Remarks</i>

Tuesday Morning Session, May 9

8:55 am – 12:15 pm

Distances and Time Regimes of Intermolecular Forces and their Impact in Materials Behavior (Part I)

Chair: Professor Norma Alcantar; co-Chair: Professor Tomas Viveros

7:30 am		<i>Breakfast</i>
8:55 am		<i>Introduction</i>
9:00 am		Decoupling of Hydrodynamic and Conservative Forces in Colloid Dynamics. Magdaleno Medina-Noyola
9:25 am		Dynamic Adhesion and Cracking Properties of Surfaces and Films on Micro and Nano Scales. Boxin Zhao
9:50 am		Friction and Lubrication in Thin Hydrogel Layers. Eugenia Kumacheva
10:15 am –	10:30 am	<i>Coffee Break</i>
10:30 am		Nanowires, Nanorods and between them: Surfactant Mediated Synthesis and Assembly of Nanostructures. Yuval Golan
10:55 am		Dynamics in Confining Nanoparticle Systems. Mustafa Akbulut
11:20 am		Unorthodox Properties of Large Critical Clusters. Alberto Robledo
11:45 am		<i>Panel Discussion</i>
12:10 pm –	12:15 pm	<i>Final Remarks and Session Closing</i>

12:30 pm		<i>Lunch Break</i>
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Tuesday Afternoon Session, May 9

3:25 pm – 5:00 pm

Distances and Time Regimes of Intermolecular Forces and their Impact in Materials Behavior (Part II)

Chair: Professor Norma Alcantar; co-Chair: Professor Tomas Viveros

3:25 pm		<i>Introduction</i>
3:30 pm		Rheology of Complex Fluids. Octavio Manero
3:50 pm		Interfacial Water on a Nanoscale. Alenka Luzar
4:10 pm		Surface Interactions and Conformations of Adsorbed Alpha Helices. José Campos-Terán
4:30 pm		The Effect of Fiber-matrix Interfacial Optimization on the Mechanical Properties of Green Composites. Pedro J. Herrera-Franco
4:50 pm –	5:00 pm	<i>Final Remarks and Session Closing</i>

5:00 pm		<i>Dinner</i>
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Tuesday Evening Session, May 9

6:30 pm – 8:30 pm

Bridging Nanoscale Forces and Interfacial Phenomena with the Macroscopic World

Chair: Professor Suzanne Giasson; co-Chair: Professor Norma Alcantar

6:30 pm –	8:30 pm	<i>Poster Session and Social Event</i>
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Wednesday Morning Session, May 10

8:55 am – 12:15 pm

Intermolecular Forces between Biomolecules and Their Role in Interfacial Phenomena of Biological Systems

Chair: Professor Joyce Wong; co-Chair: Professor Deborah Leckband

7:30 am		<i>Breakfast</i>
8:55 am		<i>Introduction</i>
9:00 am		Chemistry of Biological adhesion. Deborah Leckband
9:25 am		Membrane Adhesion: The Role of Spacers and Ligand-Receptor Bond Strength. Tonya Kuhl
9:50 am		Bridging Receptor-tethered Ligand Interactions to the Macroscopic World. Joyce Wong
10:15 am –	10:30 am	<i>Coffee Break</i>
10:30 am		Spontaneous and Reversible Switch from Amphiphilic to Oil-Like Structures. Eric Perez
10:55 am		Charge, hydration, and friction under water: a paradigm for biolubrication. Jacob Klein
11:20 am		Charge Quantization Effects on the Interactions Between Highly Charged Surfaces. Philip Pincus
11:45 am		<i>Panel Discussion</i>
12:10 pm –	12:15 pm	<i>Final Remarks and Session Closing</i>

12:30 pm		<i>Lunch Break</i>
12:30 pm –	6:00 pm	<i>Tulum and Xel-ha Tour (Lunch box will be provided to participants)</i>

Wednesday Evening Event, May 10

7:00 pm

7:00 pm		<i>Banquet Dinner</i>
7:30 pm		The Force be with JNI. Len Fisher (Key Note Speaker)

Thursday Morning Session, May 11

8:55 am – 12:15 pm

Adhesion and Tribological Properties of Films and their Impact in Macroscopic Performance

Professor Suzanne Giasson; co-Chair: Professor Octavio Manero Brito

7:30 am		<i>Breakfast</i>
8:55 am		<i>Introduction</i>
9:00 am		The Different Faces of Boundary Lubrication: What Nanotribology Can Learn from Rheophysics. Carlos Drummond
9:25 am		Contact, Adhesion and Friction between Rough Surfaces. Mark Robbins
9:50 am		JKR Contact Mechanics of Layered and Dissimilar Surfaces. Patricia McGuiggan
10:15 am –	10:30 am	<i>Coffee Break</i>
10:30 am		The Behavior of Lubricated Rough Surfaces under Compression and Shear. Kenny Rosenberg
10:55 am		Friction in Contacts of Different Adhesive Strength. Marina Ruths
11:20 am		Molecular Layering and Tribology of Poly(dimethylsiloxane) Melt in Confinement. Shinji Yamada
11:45 am		<i>Panel Discussion</i>
12:10 pm –	12:15 pm	<i>Final Remarks and Session Closing</i>
12:30 pm		<i>Lunch Break</i>
12:30 pm –	5:00 pm	<i>Free Time</i>
5:00 pm		<i>Dinner</i>

Thursday Evening Session, May 11

6:25 pm – 9:00 pm

Frontiers in Intermolecular Forces and Interfacial Phenomena (Part II)

Chair: Professor Jacob Israelachvili; co-Chair: Professor Philip Pincus

6:55 pm		<i>Introduction</i>
7:00 pm		Extension of SFA Techniques to Investigations of Fluid Interfaces. Roger Horn
7:25 pm		Theoretical Analysis of Dynamic Force Measurements Involving Deformable Drops and Interfaces. Derek Chan
7:50 pm		Nanohydrodynamics: Investigating Boundary Flows with Surface Force Experiments. Élisabeth Charlaix
8:15 pm		Microrheology from Rotational Diffusion of Colloids. Jose Luis Arauz Lara
8:40 pm –		<i>Panel Discussion</i>
9:10 pm	9:15 pm	<i>Final Remarks and Session Closing</i>

Friday Morning Session, May 12
8:55 am – 12:15 pm
Intermolecular Forces and Interfacial Phenomena affecting Structure and
Properties of Thin Liquid Films

Chair: Professor Roger Horn; co-Chair: Professor Dan Schwartz

7:30 am		<i>Breakfast</i>
8:55 am		<i>Introduction</i>
9:00 am		Using Colloidal Suspensions to Model Atomic Scale Plasticity and Lubrication Phenomena. Itai Cohen
9:25 am		Adsorption from Binary Fluids - The Transition from Critical to van der Waals Wetting. Hugo Christenson
9:50 am		The Role and Measurement of Disjoining Pressure in Lubricant Nano-Films. Lee White
10:15 am –	10:30 am	<i>Coffee Break</i>
10:30 am		Film Drainage at Deformable Interfaces - An Exotic Cocktail of Surface Forces and Hydrodynamics. Michelle Gee
10:55 am		Hydrophobic Interactions at Long and Short Range. Emily Meyer
11:20 am		Bound Water in AOT Reverse Micelles and DPPC Vesicles. Michel Picquart
11:45 am		<i>Panel Discussion</i>
12:10 pm –	12:15 pm	<i>Final Remarks and Meeting Adjourns</i>

KEY NOTE SPEAKER:

Banquet Dinner

Wednesday Evening Event, May 10, 2006, 7:00 pm

Cancún, México

The Force be with JNI

Len Fisher

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Jacob Israelachvili arrived in Australia in 1974 as a novelty – an experimentalist in a Department of Applied Mathematics. He left in 1986 as a celebrity – the inventor of the Surface Forces Apparatus, the originator of a new theory of micellar structure, and much else besides. I was lucky enough to be one of his collaborators during that exciting and memorable period. Here I tell some of the stories that did not make it into the published papers, and reveal the impact that Jacob had on those around him and on the development of colloid and surface science during that time.

ABSTRACTS:

SESSION 1

Nanoscale Forces and Interfacial Phenomena in Soft Materials

Chair: Professor Tonya Kuhl; co-Chair: Professor Matthew Tirrell

This session will focus on understanding structures and assembling of soft materials such as polymers and nonbiological self-assembly systems. This area will address the study of the large structures, scale processes, developing novel tools for measurement and manufacturing at the nanoscale, developing novel concepts for high-rate synthesis and processing of soft materials. Examples of presentations include synthesis, fabrication methods for devices and polymeric systems, design concepts for manufacturing, simulation of the manufacturing methods and the effects of intermolecular forces. Possible benefits include improving the understanding of structure interfacial phenomena that will resulted by different synthetic and manufacturing processes in the pre-competitive environment. The information of this area will increase the performance and scale up of promising novel and composite soft materials.

Hard and Soft Nano-Junctions

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Investigations of physical systems of small sizes and reduced dimensionalities open avenues for systematic explorations of the physical factors and unifying principles that underlie the transition from the atomic and molecular domain to the condensed phase regime. Such behavior, where the properties do not scale with the reduced physical size, but rather where *Small is Different* in an essential way that can not be deduced through extrapolation from knowledge of bulk behavior, is emergent in nature.

Computationally-based modeling and simulations play an increasingly important role in modern condensed matter physics, chemistry, materials science, and biology [1]. In particular, such studies, allow explorations of complex phenomena with refined resolution in space and time. Furthermore, in some occasions atomistic simulations may be regarded, and used, as numerical experiments whose analysis guides formulation of new theoretical treatments of continuum nature.

In this talk we focus on formation processes and properties of nanoscale junctions. We discuss first *hard junctions* – that is, interfacial nanowires formed when two surfaces are brought close to contact, or as a result of contact separation. Such nanowire junctions are implicated as underlying frictional resistance, and they exhibit unique mechanical (dislocation-less response) and electrical (quantized conductance) characteristics. Subsequently, we discuss *soft junctions* – that is, lubricated nano-junctions and liquid nanobridges. We illustrate the occurrence (or absence) of layering transitions and oscillatory solvation forces for morphologically smooth and atomically rough confinements, and present results from most recent investigations addressing the behavior of water under highly confined conditions.

1. U. Landman, “Materials by Numbers: Computations as Tools of Discovery”, perspective article in Proc. Nat. Acad. Sci. (USA) **102**, 6671 (2005).

Structural Forces at Aqueous Interfaces

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Water provides the matrix of many bio-molecular mechanisms. Looking at the many remarkable macroscopic properties of water, which are often related to the dipole and H-bond interactions of the molecule, the question is justified whether water can form extended transient structures in molecular complexes, near interfaces or even in its bulk. Suggested structural models - some of them were disproved - include everything from poly-water to various forms of clustered water. Although we can hardly determine the details of the water structure via a direct force measurement, it is widely accepted that the entropy term of water controls many macromolecular interactions (c.f. hydrophobic attraction). We have investigated a water-soluble polymer grafted to a surface and detect the expected steric repulsion from the polymer brush. High-resolution force measurements, however, allow one to detect an additional fine structure that suggest the existence of an extended equilibrium water structure subtly embedded into this the polymer layer. The relevance of this water structure to the phenomenon of protein-resistance is discussed. An outlook is presented that discusses ongoing efforts to detect long-range structural forces in bulk water using a modified eSFA setup. These efforts are put in relation to the known hydration forces observed previously in the presence of adsorbed ions on the mica surface.

Selective Coalescence of Bubbles in Simple Electrolytes

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Recent experimental and theoretical work found that different ions in aqueous electrolyte solutions have very specific affinities for the approach to the water/air interface. This behaviour leads to the formation of surface layers with depleted or enhanced concentrations of charge and sometimes to the formation of electrical double layers. We propose to describe the formation and interaction of surface layers using effective potentials between ions in a solution and between ions and the surface. The potentials are obtained via a reverse Monte Carlo procedure from the simulations of full aqueous solutions and they efficiently account for the solvent degrees of freedom. The electrostatic effects are particularly interesting because of the role they play in the interaction between free surfaces or between hydrophobic aqueous interfaces in electrolytes. One such example is the foaming of sea waves that is very different from the rapid fusion of bubbles in fresh water. We specifically describe two qualitatively different examples: (i) surface concentration of anion is enhanced and cation depleted (NaCl solutions) leading to the electrical double layer repulsion of surfaces and inhibition of bubble fusion; (ii) concentration of both anion and cation is enhanced (HCl solutions), leading to ionic correlation attraction between surfaces and the easy fusion of bubbles. Comparison with the empirical rules for bubble fusion discovered by Craig, Ninham and Pashley in 1993 indicates that the controlling property is the propensity of each ions for the free surface of water and that the fusion is inhibited in cases where a weak double layer forms at the solution surface.

Surfactant Interactions with Polyelectrolytes: Microscopic Binding and Macroscopic Gel Particles

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Mixing of oppositely charged surfactants and polyelectrolytes in aqueous solutions leads to surfactant adsorption onto the polyelectrolyte chain. The binding isotherm is usually measured with an ion-selective electrode, which requires time-consuming experiments with sensitive, custom-built equipment. Here we present a simple method for approximating binding isotherms from isothermal titration calorimetry (ITC) data. The results suggest some conditions favor the formation of intrapolymer surfactant aggregates, while others promote the formation of interpolymer surfactant/polyelectrolyte networks. Regardless of the nature of the binding, mixing of oppositely charged surfactants and polyelectrolytes in aqueous solutions can lead to associative phase separation, where the concentrated phase assumes the form of a viscous liquid, gel, or precipitate. This phenomenon can lead to the formation of gel-like particles whose size and polydispersity can be controlled. Specifically we show here present phase behavior and structural studies of gel-like particles formed by mixing drops of N,N,N-trimethylammonium derivatized hydroxyethyl cellulose (JR-400) polyelectrolyte solution with oppositely charged anionic and cationic surfactant solutions composed of sodium perfluorooctanoate and cetyltrimethylammonium bromide. Gel formation apparently occurs due to the collapse of the polyelectrolyte chains upon the adsorption of surfactant. This process results in the release of simple ions and water, and yields dense gel-like beads. The diameter of these beads ranges approximately from 200 to 4000 microns. Both the effects of solution composition and the method of preparation are studied by optical and confocal microscopy, and are linked to the structure and stability of the bead. Our observations suggest that the structure of the resulting particles is governed by the solution composition and the method of preparation, while the particle stability is governed by phase behavior alone.

Direct Measurement of Adhesion between Identical Polyelectrolyte Brush Layers in the Presence of Multivalent Counterions

Feng Li and Matthew Tirrell

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The interaction between brushes of sodium poly(styrenesulfonate) (PSS), a strong polyelectrolyte, in the presence of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB, $\text{cmc} = 10^{-3}$ M) was studied using a surface force apparatus (SFA). The brushes were formed by adsorption of di-block copolymers of PSS and a hydrophobic block, poly(tert-butylstyrene). As the concentration of CTAB in bulk solution was increased from zero, the brushes began to contract at very low surfactant concentrations, in the neighborhood of 10^{-6} M. Attractive forces were observed above 10^{-4} M CTAB after the two brush surfaces came into contact. The brush contraction and the appearance of attractive force did not reverse even after CTAB in bulk solution was diluted, which means that the adsorption of CTAB to brushes is at least partially irreversible. It was also found that the strength of the measured attractive forces increases on the dilution of CTAB in the surrounding bulk solution. The combination of data on force of interaction with measurement of brush dimensions gives a clearer picture of the origins of observed behavior. This pattern of behaviors of brushes indicates the formation of a series of aggregated structures of CTAB within the brushes, which in turn produce a multi-valent electrostatic attraction among the PSS segments, leading to brush contraction and inter-brush attraction.

Behavior of End-Grafted Charged Polymers

*Mohan Surchabesan¹, Benoît Liberelle², Béatrice Lego², Armand Soldera³ and
Suzanne Giasson^{1,2}*

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End-grafted charged polymers, or charged brushes, can be used to control and modify surface properties such as adhesion, lubricity, biocompatibility, colloidal stability. The normal and lateral forces between two opposing and moving surfaces bearing charged brushes have been extensively investigated, both experimentally and theoretically, by several groups. When two opposing charged brushes are compressed and sheared, entropic factors associated with the counterions result in less interpenetration, stronger repulsive forces and lower friction coefficient relative to neutral brushes. However, little attention has been given to the factors controlling interpenetration between opposing charged brushes. In order to correlate molecular properties of charged brushes (i.e. degree of ionization, molecular weight, surface grafting density, conformation) with their behaviour (interpenetration thickness upon compression and resulting shear force between two sliding opposing brushes) we used a meso-scale simulation approach. Our simulation results agree very well with previous experimental and theoretical data. Simulations show that friction coefficient is directly correlated with the extent of the interpenetration between two opposing sliding brushes. In addition, our simulations allow the interpenetration thickness to be quantified and correlated with compression ratio, degree of ionization as well as distribution of charges along the polymer chain, ionic strength of the media and valence and size of added ions.

In order to validate our simulations, we have constructed polyelectrolyte brushes, irreversibly attached onto mica surfaces, using “graft-to” and “graft-from” approaches. For both cases, mica substrates were initially activated under water plasma to create surface hydroxyl groups. The graft-to approach consists of attaching a PS-b-X (polystyrene-b-polyelectrolyte) diblock copolymer to a thin PS film covalently attached to OH-functionalized mica surfaces. For the graft-from approach, we used ATRP to grow polymer brushes onto initiator-grafted mica substrates (the initiator is covalently attached to OH-functionalized mica substrates). We have used

ellipsometry, water contact angle, AFM and SFA to characterize the brushes. Measurements of normal and frictional forces between opposing brushes are under progress.

SESSION 2

Frontiers in Intermolecular Forces and Interfacial Phenomena Parts I and II

Chair: Professor Jacob Israelachvili; co-Chair: Professor Philip Pincus

Intermolecular forces and interfacial phenomena are responsible of the functionality of materials, devices, and systems with novel properties and functions that are achieved through the control of matter, molecule by molecule, surface by surface or at the macromolecular level. A revolution has begun in science, engineering and technology, based on the ability to organize, characterize, and manipulate matter systematically at levels where controlling intermolecular forces becomes extremely valuable and useful to understanding complex and conventional materials. Far-reaching outcomes for the 21st century in these two areas are envisioned in both scientific knowledge and a wide range of technologies in most industries, healthcare, conservation of materials and energy, biology, environment and education. Opportunities have opened as new tools enable fundamental discoveries and technological advances. Outstanding benefits have resulted from initial studies and applications. Formidable challenges remain, however, in the areas of fundamental understanding, device design, system design and architecture, manufacturing, and system integration and deployment taking into account the intermolecular forces, interfacial phenomena, and education.

Extending the Range and Scope of Surface Force Measuring Techniques

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Recently introduced attachments to the SFA will be described, as well as suggestions for future innovations for expanding the scope of surface force measurements. These advances will include displacement and simultaneous measurement of forces in three orthogonal directions, high speed dynamic (e.g., friction, shear) measurements, combining the SFA and AFM techniques in one instrument, and interfacing SFA with other types of in situ measurements such as x-ray and spectroscopic measurements.

Shedding Light on the Dark Side of Surface Forces

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The development of the Surface Forces Apparatus (SFA) by Israelachvili and coworkers in the 1970's led to the first accurate measurement of surface forces, and stimulated a rapid discovery of new and interesting colloidal science. In the 1990's, the Atomic Force Microscope (AFM) emerged as a valuable and popular technique for surface forces measurements, particularly when employed with a large spherical colloidal particle ($r \sim 3 \mu\text{m}$) attached to the force sensor (the 'colloid probe' technique). However, the interpretation of colloidal probe measurements is not unambiguous: the absolute separation between the surfaces is not measured explicitly, but is inferred from the force measurement. In particular, with the colloidal probe technique it is not possible to establish a constant reference condition for the zero of separation in a series of approaches between the surfaces. In this talk I describe an alteration to the colloidal probe technique in which the separation is explicitly determined from the scattering of an evanescent wave that is generated at the surface of the solid sample. Using this technique, we have sifted through some established areas of colloid probe research, hydrodynamic forces, polymer forces and hydration forces, and find that some new conclusions emerge. In addition, we find significant deviations from the scattering profile that is usually assumed in Total Internal Reflectance Microscopy, which should lead to a reexamination of some results produced by that technique.

Using Intermolecular Forces and Interfacial Phenomena to Help Humanity

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Understanding intermolecular interactions is paramount to predicting the behavior and characteristics of materials. This talk will discuss the relationship between surface forces, surface chemistry, and the performance of nanostructured materials in three areas: 1. Smart drug delivery for brain tumors; 2. Natural and environmentally benign agents for the treatment of drinking water; and 3. Insights into surface-attached plaques associated with Alzheimer's disease..

A Three Component Force Transducer for Atomic Force Microscopy

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A new instrument has been designed and built that can simultaneously measure the force in 3 directions. The 3-D force microscope consists of a unique strain gauge pattern attached to a force measuring spring. Finite element modeling (FEM) has been performed to optimize the design configuration. The instrument can be fitted into the SFA, enabling in situ topography and other physical measurements such as friction. A micromachined version of the device can also be used as an atomic force microscope. Results will be presented of the FEM analysis, sensitivity of the device, and initial measurements of rheology and friction.

Extension of SFA Techniques to Investigations of Fluid Interfaces

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A surface force apparatus (SFA) at the University of South Australia has been modified to replace the upper cylindrical mica surface by a flat one and the lower surface by a fluid drop held at the end of a fixed capillary. The FECO spectrum is examined after light incident from above is reflected from the surfaces, instead of the usual arrangement using transmitted light. This enables the mica-fluid separation to be determined, and most importantly, the drop surface profile to be recorded. Deformation of the fluid drop when it interacts with the mica surface under static or dynamic conditions provides key information about the interaction, as will be demonstrated in this talk. Initial experiments were carried out with a mercury drop immersed in aqueous electrolyte solution. Benefits of using mercury as a model fluid for these studies include its high reflectivity, its high interfacial tension with water creating a smooth surface, and its status as a near-ideal polarisable electrode for classical electrochemical investigations. Furthermore, an electrical potential can be applied to mercury to control its surface charge, thereby giving the experimenter control over the double-layer forces between the drop and the mica surface. Subsequent experiments have investigated the behaviour of an air bubble approaching mica in water (or electrolyte). The sharpness of the FECO fringes and hence the resolution in measuring the thickness of the aqueous layer depends on the reflectivity of the interface between the background fluid (water) and the drop/bubble. In the case of mercury, its high reflectivity gives a resolution of around 0.3 nm, whereas the lower reflectivity of the air/water interface results in a resolution of around 1.0 nm. Data will be presented showing how drop (or bubble) deformation depends on the surface and hydrodynamic forces as it is approached by a flat mica surface. One of the possible ways to analyze the data is to calculate the interfacial curvature from the measured drop shape, and use this to calculate the local pressure difference across the interface. Given that the pressure inside the drop (bubble) is essentially constant, it is simple to find the pressure in the aqueous film that

separates it from the mica, at all radial positions and times throughout an experimental run. This pressure can be integrated to find the total force acting on the drop/bubble. The pressure includes hydrodynamic pressure, and disjoining pressure which in our experiments is attributable mainly to double-layer forces. If the disjoining pressure is a known function of the aqueous thickness, it can be subtracted from the total film pressure to give an experimental determination of hydrodynamic pressure in a draining film. Illustrative results will be presented showing some of the equilibrium and nonequilibrium pressures that have been measured with mercury drops and with air bubbles interacting with mica in an aqueous medium.

Theoretical Analysis of Dynamic Force Measurements Involving Deformable Drops and Interfaces

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Dynamic or velocity dependent forces between surfactant and polymer stabilised deformable oil drops of ~ 50 μm radius have been measured using the Atomic Force Microscope (AFM) under a range of velocities and aqueous solution conditions. At a different length scale, a modified version of the Surface Force Apparatus (SFA) has been used to visualise the deformation of a mercury/solution interface (2mm radius) upon the approach or retraction of a planar mica surface under a range of velocity and displacement schedules. In both AFM and SFA studies, the interfaces deform under the combined action of well controlled and known colloidal surface forces and hydrodynamic forces arising from fluid movement in the thin film between the moving and interacting surfaces. In addition to the familiar dimpling of deformable interfaces under approach, other exotic deformation modes are possible under more complex velocity and displacement schedules. A detailed theoretical model that incorporates surface forces, hydrodynamic interactions and surface deformations has been developed that accounts self-consistently for the coupling of such effects in determining the dynamic force and surface deformations during the approach and retraction phases of AFM and SFA measurement. The model gives very good quantitative agreement for the force as well as the variation of surface deformations with position and time. In addition, the models also provide information about the velocity profile of the deforming interfaces as each stage of the interaction.

Nanohydrodynamics: Investigating Boundary Flow with Surface Force Experiments

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The investigation of fluid flows at a small scale is a particularly active field. Many new applications, beyond the classical area of tribology, have emerged recently. Manipulation of small quantities of liquid in microfluidic devices, flow around biological objects, lubrication in joints, transport of colloids by electrokinetic effects, are crucially dependent on the interfacial friction between solid and liquid.

A number of experimental techniques have been used to study interfacial flows. However, while it is now admitted that simple liquids may undergo substantial slip on solid surfaces, experimental studies of boundary flows have not provided a consensual picture. Slip effects reported vary quantitatively as well as qualitatively regarding their variation with the shear rate, with no clear cut relation with relevant surface parameters such as interactions or roughness.

In this talk I will show that the use of surface force apparatus in the dynamic mode can bring new highlights in this domain. I will first discuss the intrinsic boundary condition of water on smooth surfaces using various hydrophilic and hydrophobic surfaces, and show that intrinsic slip occurs on hydrophobic surfaces but remains of moderate amplitude under ambient conditions. Then I will study the influence of the liquid viscosity, using water-glycerol mixtures, with respect to the model of the "gaz layer" trapped at the solid-liquid interface. Finally I will present first results on textured superhydrophobic surfaces. On this structured surfaces I will show that the presence of tailored trapped bubbles allows to monitor both the boundary flow and the surface elasticity in a controlled way.

Microrheology from Rotational Diffusion of Colloidal Particles

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The microrheology of viscoelastic fluids is obtained from rotational diffusion of optically anisotropic spherical colloidal probes, measured by depolarized dynamic light scattering. The displacement is in excellent agreement with those obtained from translational diffusion and by mechanical measurements. We also show that this method is applicable to samples with strong light scattering components. This extends the capabilities of the microrheological methods based on the diffusional motion of colloidal probes.

SESSION 3

Distances and Time Regimes of Intermolecular Forces and their Impact in Materials Behavior Part I and II

Chair: Professor Norma Alcantar; co-Chair: Professor Tomas Viveros

New concepts and design methodologies in Materials Science will be discussed and disseminated in this session. Additional topics include the creation of new devices, the synthesis of materials systems and integration of materials into architectures for various operational environments. These require a profound understanding of the physical, chemical, and biological interactions among the intermolecular forces and interfacial components. In order to systematically design complex materials systems, multiple layers of abstractions and various mathematical models to represent component behavior in different layers will also be exploited. Presentations in this session include the development of new tools for sensing, assembling, processing, manipulating, manufacturing and integration along scales, controlling and testing the structures, devices, design and architecture of concepts, software specialized for metals, ceramics, and composite materials. One can envision materials systems that sense and gather information and analyze and react to that information, and architectures, and novel separation systems with intermolecular and interfacial resolution.

Decoupling of Hydrodynamic and Conservative Forces in Colloid Dynamics

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Hydrodynamic interactions are many-body, solvent-mediated forces, whose long range and non-conservative character makes the theoretical description of their effects at intermediate and long times a most involved problem in the field of colloid dynamics. In this contribution, we present a self-consistent statistical mechanical theory of the dynamic properties of colloidal dispersions, which allows for the description of the dynamic properties of systems with strong or complex hydrodynamic interactions. The predictions of this theory are compared with the experimental measurements of the relaxation of concentration fluctuations (represented by the van Hove function) for suspensions confined between two parallel plates.

Dynamic Adhesion and Cracking Properties of Surfaces and Films on Micro and Nano Scales

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Dynamic adhesion and fracture behaviors of surfaces and films are studied in the Surface Forces Apparatus using the 'FECO' optical interference technique which allows one to observe surface shape changes on micro and nano scales. In particular, transitional behaviors are investigated when surfaces or films change from liquid-like to solid-like states. We will address the micromechanical properties of liquid and solid surfaces and types of instabilities observed during their approach, contact and detachment, and discuss common situations where similar effects likely occur.

Friction and Lubrication in Thin Hydrogel Layers

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Low friction in thin layers of hydrogels is vital in the design and production of artificial organs, cartilages, contact lenses, or artificial tears. We used a surface force apparatus with shear capability to examine the normal and shear forces in confined hydrogel layers. Our work proceeded in two directions. First, we examined the mechanism of lubrication that was caused by shear thinning of thermoreversible polymer hydrogels. For the gels formed by linear synthetic water-soluble polymers bearing hydrophobic groups at two ends (telechelic polymers), shear thinning resulted in very weak shear forces, with the effective friction coefficient $\mu < 0.04$. At strong compression of the gel the shear forces gradually increased due to the compression-forced interpenetration and entanglement of the macromolecules and interactions between the hydrophobic groups.

Second, we examined the change in adhesion and friction in thin hydrogel layers in response to the change in ambient humidity. The study was conducted for polysaccharides such as hydroxymethyl cellulose and carboxymethyl cellulose. For the first polymer we show how adhesion between the layers develops when they are exposed to increasing humidity. For the second polymer we demonstrate increasing friction and the change in nature of shear response when the ambient humidity decreases.

Nanowires, Nanorods and between Them: Surfactant Mediated Synthesis and Assembly of Nanostructures

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Semiconductor nanostructures with well-defined shapes and sizes are considered to be the main building blocks of future nano-devices. A simple bench-top synthesis for the preparation of such nanostructures is presented for the preparation of highly uniform wires and rods of ZnS and ZnSe with ultra-narrow widths and well-controlled aspect ratios. The synthesis makes use of a single xanthate salt precursor molecule which is dissolved in molten alkyl amine surfactant and decomposes under mild laboratory conditions to give the desired II-VI semiconductor material. The role of the surfactant in determining the shape, size and structure of the nanostructures is demonstrated. In particular, surfactant mediated assembly into highly ordered super-structured arrays in 2D and 3D is investigated using a variety of complementary in-situ and ex-situ techniques.

Dynamics in Confining Nanoparticle Systems

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The normal and lateral forces between mica surfaces confining dodecane solutions of various shapes, concentrations and sizes of functionalized nanoparticles were measured under a variety of conditions. The normal forces were roughly logarithmically repulsive at short distances and roughly linear at large distances. However, the distance at which repulsion was felt strongly depended on shape, concentration, and size of nanoparticles. The lateral forces also strongly depended on these factors: Nanorods and nanowires can provide both low friction and good surface wear protection. On the other hand, nanospheres had poor lubrication properties compared to others. The superior properties of nanorods and nanowires are due to a combination of the nanoparticle geometry (short rods or wires rather than spheres), nanoparticle stiffness (hard, robust cores with soft outer layers), and nanoparticle interactions (weakly adhesive inter-nanoparticle and nanoparticle-surface forces due to a synergy between the nanoparticle cores, the surfactant layers, the solvent, and the surfaces).

Unorthodox Properties of Large Critical Clusters

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We examine the properties of order parameter clusters at criticality and consider their significance to statistical-mechanical ground rules. These properties are obtained through a technique similar to the density functional approach for stationary inhomogeneities in fluids at equilibrium. We present both static and dynamical aspects of a single large cluster and describe these in terms of the laminar episodes of intermittency. A comparison is made with the standard surface properties of small droplets and thin films.

Rheology of Complex Fluids

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The dynamics of complex fluids, specifically micellar solutions and associative polymers, are described in this presentation. Experimental data are analyzed with rheological models that couple a constitutive equation of state with an equation representing the structure modification due to the flow. Furthermore, attention is given to a model that includes two coupled kinetic processes to describe the rheological behavior of complex fluids. Five microstates are defined, representing the complexity of interactions among the macromolecules suspended in a Newtonian fluid. These microstates represent statistically networks with varying entanglement density. It is assumed that the energy barrier required to modify the complexity of the system can be provided by the flow, and that the flow-induced change in the network complexity is modeled as a coupled kinetic scheme constituted by a set of reversible kinetic equations describing the evolution of the microstates. The average concentration of microstates at a given time defines the maximum segment length joining the entanglement points in the transient network. The rheological material functions are calculated according to the classical statistical description of a transient network, but with a variable maximum segment length (variable extensibility) which is a function of the kinetics of the microstates. The model predicts time-dependent non-linear rheological phenomena, such as thixotropy, stretched exponential relaxation and other interesting responses of complex fluids.

Interfacial Water on a Nanoscale

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The talk will discuss our general understanding of the phase behavior of interfacial and confined water, kinetic aspects of self-assembly, and the elementary mechanisms involved in solvent-induced interactions between synthetic and biological solutes in aqueous environment. I will discuss recent theoretical progress on understanding the influences of dissolved gases on dewetting, and electric field effects on interfacial tension, providing new insights to relevant applications on nanoscale, e. g. ion channels and microfluidics.

Surface Interactions and Conformations of Adsorbed Alpha Helices

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Interaction between amphiphilic α -helical proteins (human apolipoprotein AII) adsorbed on a hydrophilic surface from a buffer solution at pH 4 was studied, using an interferometric surface force apparatus. The interaction forces between the adsorbed layers of α -helices are mainly composed of electrostatic double layer forces at large surface distances and of steric repulsive forces at small distances. Amphiphilicity of the α -helix structure facilitates the formation of protein multilayers next to the surfaces. We also found that the interaction mica-protein is stronger than protein-protein interaction. The results of protein adsorption and force interaction suggest that they are consequences of the protein secondary structure, the amphiphilic α -helix motif.

The Effect of Fiber-Matrix Interfacial Optimization on the Mechanical Properties of Green Composites

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Cellulosic fibers are readily available from natural sources and most important, they have a low cost per unit volume. One difficulty that has prevented a more extended utilization of natural fibers, in special applications, for example as a reinforcing material to most polymeric matrices is the lack of good adhesion between them. It is well known that natural fibers impart polymeric matrix composites high specific stiffness and strength, a desirable fiber-aspect ratio and biodegradability. The hydrophilic nature of natural fibers adversely affects adhesion to a hydrophobic matrix resulting in poor strength properties. Different approaches to improve fiber-matrix adhesion are explored for a specific fiber-matrix system, namely, henequen fibers (*Agave fourcroydes*) and a thermoplastic matrix, high density polyethylene (HDPE). Both, the mechanical and the chemical aspects of fiber surface modification are presented. The interfacial shear strength (IFSS) between the natural fibers and the thermoplastic matrix was improved by morphological and chemical modifications of the fiber surface. The surface physicochemical properties were optimized and the effect was reflected on the material as higher interfacial shear strength values. This IFSS was measured using micromechanical techniques, such as the single fiber fragmentation test. The effect of the fiber surface treatment optimization was also related to the effective mechanical properties of the laminated material.

SESSION 4

Intermolecular Forces between Biomolecules and Their Role in Interfacial Phenomena of Biological Systems

Chair: Professor Joyce Wong; co-Chair: Professor Deborah Leckband

This area supports the presentation of the development of a fundamental understanding of biostructures and processes, biotechnology, and techniques for a broad range of applications in biomaterials, biosystem-based electronics, agriculture, energy, and health. This area promotes the progress in the study of biological and biologically inspired systems in which nanoscale forces and interfacial phenomena play an important role. This includes developing an understanding of the relationships among chemical composition, molecular behavior, and physical shape at the nanoscale and biological function. Additional research areas include the study of hydrophobic and hydrophilic interactions with organelles and subcellular complexes, and the effects of intermolecular forces in the synthesis of biomedical materials based on the principles of biological self-assembly. This session will also include the study of forces, interfacial phenomena, and their role in bioprocessing manufacture products, including novel biomaterials, improved delivery of bioactive molecules, nanoscale sensory systems, biochips, and the modification of existing biomolecular machines for new functions.

Chemistry of Bioadhesion

Deborah Leckband

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The adhesive strength of intercellular junctions in biology is determined by the large numbers of protein binders on cell membranes. A fundamental question is how the chemistry of these bonds determines the mechanical strength of the resulting junctions. We are using a multi-scale approach to establish molecular design rules in biological adhesion. Using the Surface Force Apparatus, we quantify the strength of receptor-mediated adhesion and identify possible functional connections between the protein architecture and biological function. Chemical interactions governing the protein adhesive strengths were identified using steered molecular dynamics simulations. Force measurements with mutants generated on the basis of the simulations further identified correlations between adhesion strength and the thermodynamic and kinetic properties of these individual biomolecular bonds. These investigations are uncovering the fundamental design rules that govern the functions of these important molecules in vivo and in vitro.

Membrane Adhesion: The Role of Spacers and Ligand-Receptor Bond Strength

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Much experimental and theoretical effort has been directed at elucidating the forces and dynamics of breaking, rupturing or unbinding ligand-receptor bonds, e.g., measuring the bond strength as a function of pulling rate or time using a variety of techniques. In contrast, much less attention has been given to the formation of ligand-receptor bonds. Using a combination of theory (analytical and simulations) and direct experiments (using the Surface Forces Apparatus technique) of a polymer tethered ligand receptor system, we have quantified the way polymer chain dynamics, ligand-receptor binding strength, tethered architecture, and grafting density determine the spatial range, capture time, and subsequent adhesion of complementary surfaces. Also explored are the tethering chains' nonspecific repulsive interactions with model membranes, their adhesion under flow, and implications for targeting polymer-coated particles towards biomimetic surfaces and cells. Methods for tailoring specific adhesion without altering the ligand-receptor bond strength will be highlighted.

Bridging Receptor-tethered Ligand Interactions to the Macroscopic World

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A major challenge in developing clinically-useful drug carriers or imaging contrast agents lies in achieving specific binding with intended targets while at the same time avoiding recognition by the immune system. Targeted delivery of therapeutics would greatly impact the pharmaceutical industry by allowing the use of drugs currently shelved because of detrimental side effects. Equally as important, the development of targeted contrast agents would greatly facilitate early detection of disease. Traditionally carriers have been tested in either animal models or cell culture static binding studies. Here we describe a model in vitro system to investigate how physiologically-relevant PEGylation conditions (5 mol% polyethylene glycol) affect carrier binding properties under flow. Physiological flow is a critical parameter that impacts targeting because of the natural variation of flow in the different types of arteries and veins in the circulation.

Two key and novel aspects of our flow system are high-throughput screening and quantitative trajectory analysis. We integrate microfluidic patterning with flow chamber methodologies to directly compare receptor/ligand binding to varying carrier surface compositions under identical flow conditions. We use streptavidin and PEG-tethered biotin and biotin analogs as a model system because it is well-studied and is readily adapted to incorporate physiologically-relevant ligands. We will discuss our results of velocity before arrest, binding frequency, arrest duration, and particle detachment resistance to flow. In particular, we find that in addition to ligand accessibility and concentration, particle dynamics and Brownian motion play a critical role in setting the binding distance range.

Spontaneous and Reversible Switch from Amphiphilic to Oil-Like Structures

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Whether in the fluid or gel state, lipid bilayers have a strong cohesion, which enables them to resist pressures applied locally, tensions, and curvature. Current theories assume that the amphiphilicity of biological membranes is always preserved. We observed that two hydrogen-bonding lipid layers in contact can spontaneously and reversibly lose their amphiphilic structure and turn into an assembly of oily complexes which flows under local pressure. This result opens a new angle for understanding the reorganization of lipids during membrane fusion, since similar complexes could fill the troubling hydrophobic voids displayed in the current models.

Charge, hydration, and friction under water: a paradigm for biolubrication

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To understand friction in aqueous environments, particularly at the pressures and shear rates relevant in living systems, it is essential to take account of charged state of the surfaces, the hydration layers that form about such charges, and often the flexible, charged macromolecular species coating the sliding substrates. This talk will present recent advances in this area, especially their relevance to biological lubrication as in synovial joints and other rubbing surfaces in the body.

Charge Quantization Effects on the Interactions between Highly Charged Surfaces

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The fact that charges are quantized in units of e implies that there are no truly homogeneous charged surfaces. Together with charge regulation in a Stern layer, this is the basis for the Bloomfield-Rouzina (BR) mechanism for attractive forces between highly charged surfaces. On a larger length scale, the patchiness of bilayer coated surfaces induced by the 2 dimensional Rayleigh instability also leads to even longer range attractions than in the BR mechanism. The characteristic length scale of the bilayer patches, the Solis length, is proportional to the Gouy- Chapman length of the highly charged patches.

SESSION 5

Adhesion and Tribological Properties of Films and their Impact in Macroscopic Performance

Professor Suzanne Giasson; co-Chair: Professor Octavio Manero Brito

Presentations in this area explore the novel phenomena and the role of material structures that appear at the molecular scale when they are subjected to adhesive, shear and lateral external forces. This session is critical to understand the response of overcoming obstacles to miniaturization as feature sizes in devices that have reached the nanoscale. Additional information in this area also refers to fundamental physics and chemistry aspects, development of the experimental tools necessary to characterize and measure tribological properties and their effect on structures and interfacial phenomena. It also includes the development of techniques for thin film design and molecular scale processes. It also includes investigations of molecular dynamics algorithms and means for error correction in molecular information systems. The possible benefits include molecular wear, nanostructured friction, and advanced lubricating systems.

The Different Faces of Boundary Lubrication: What Nanotribology Can Learn from Rheophysics

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Recently, rheophysics has shown that complex fluids may undergo shear-induced transitions leading to shear thinning or thickening behavior, which often are accompanied by shear banding and a complex dynamical response labeled “rheochaos”.

Qualitatively similar responses have been observed when shearing a single asperity contact, suggesting the possibility of building a closer analogy between these phenomena occurring at very different length scales. In the framework of this comparison, we will present results of nanotribological studies of a number of self-assembled surfactant-polymer systems with a Surface Forces Apparatus-nanotribometer.

Contact, Adhesion and Friction between Rough Surfaces

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Surfaces are often rough on many length scales and can be described as self-affine fractals. Contact, friction and adhesion between such surfaces have been studied using finite-element methods (FEM), molecular dynamics (MD) simulations and hybrid MD-FEM techniques. Continuum simulations reveal a complex contact morphology with power law correlations and distribution of contact sizes. The behavior is dominated by roughness at the smallest length scale. Atomistic simulations show that atomic scale roughness can lead to large deviations from continuum results, particularly for friction and adhesion. For example, the pulloff force may lie outside the bounds provided by JKR and DMT theory. Hybrid and atomistic simulations of friction between rough surfaces show that plasticity becomes important on relatively smooth surfaces, and may dominate the frictional force.

JKR Contact Mechanics of Layered and Dissimilar Surfaces

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JKR contact mechanics assumes the surfaces are homogenous and isotropic and that there is full slip at the interface. We examined the applicability of JKR theory for layered materials such as those found in the Surface Forces Apparatus (SFA). Measurements of the adhesion and deformation of two contacting, molecularly-smooth layered mica / epoxy / silica surfaces were performed using the SFA. Primary and secondary optical interference fringes were used to measure the mica and epoxy thicknesses and radii of curvature, as well as the contact diameter as a function of applied force. Nanoindentation and microindentation were used to measure the elastic properties of the individual materials and of a layered system. The loading/unloading measurements of contact radius or indentation depth are compared with the predictions of Johnson, Kendall & Roberts (JKR) adhesion theory extended to layered systems (2-layer and 3-layer) using finite element analysis. Measurements of the effective elastic modulus of the layered system compared well with the extended theory. Loading/unloading SFA measurements in the presence of adhesion showed significant hysteresis, presumably due to viscoelastic deformation in the epoxy layer. This led to the unloading contact radius/load curve to follow the JKR relationship for a homogeneous solid rather than a layered one. Furthermore, the theoretical JKR analysis of the pull-off force, F_p , for SFA experiments using crossed cylinders of radius R , where the materials are layered and the mica/mica adhesion is high, indicates that the surface energy, γ_{sv} , can vary with F_p according to $F_p / 4\pi R < \gamma_{sv} < F_p / 2\pi R$, and for this particular experiment was given as $\gamma_{sv} = F_p / 3.5 \pi R$ as compared to $\gamma_{sv} = F_p / 3 \pi R$ for homogeneous materials. Between dissimilar silica-mica materials, the contact diameter versus load is stepped due to the high friction between the two materials.

The Behaviour of Dry and Lubricated Rough Surfaces under Compression and Shear

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Using a Surface Forces Apparatus (SFA) we have studied the effects of surface roughness (root-mean-square (RMS) roughness between 0.3 and 220 nm) on the “contact mechanics” (adhesion, loading and unloading forces and deformations) and friction of various polymeric surfaces. Two different classes of rough surfaces were measured: randomly rough and patterned surfaces. An Atomic Force Microscope (AFM) was used to measure statistical roughness parameters such as the RMS or the fractal dimension. We show how the type of roughness is extremely significant in determining the qualitative behavior of the normal and frictional forces. Finally we discuss how the addition of a lubricating oil significantly modifies the forces as compared to those measured in a dry atmosphere.

Friction in Contacts of Different Adhesive Strength

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The boundary friction of different aromatic self-assembled monolayers has been measured in a single-asperity contact with the surface forces apparatus (SFA) and with an atomic force microscope (AFM). The strength of the adhesion between the sliding surfaces is altered by working in dry N₂ gas or in ethanol. Low adhesion (in ethanol) results in a linear dependence of the friction force on load already at low loads, whereas high adhesion (in N₂) gives an apparent area-dependence. The reduction of the area-dependence in ethanol allows a direct, quantitative comparison of load-and velocity-dependent friction of surfaces whose radius differs by 5-6 orders of magnitude. It is also shown that when applying a contact mechanics model developed for adhesive, layered systems by Sridhar, Johnson and Fleck to data obtained in N₂ with the AFM, it is possible to obtain critical shear stresses that agree well with data established with the SFA.

Molecular Layering and Tribology of Poly(dimethylsiloxane) Melt in Confinement

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Friction measurements were carried out for molecularly thin films of poly(dimethylsiloxane) (PDMS) melt ($M_w \approx 80000$) as a function of applied pressure and sliding velocity using the surface forces apparatus. The PDMS films exhibit apparent layering transitions when the thicknesses of the films are decreased to the order of molecular dimensions. For four-layer and three-layer films, “solid-like” sliding is observed and the shear stresses are on the order of 105 Pa. Further compression and simultaneous lateral motion squeeze out the PDMS molecules to a final residual film two molecular layers in thickness, whose shear properties include “viscous” characters and the shear stress increases abruptly by a factor of 6-8. This shear property change may arise from the different sliding mechanisms of “adsorbed” and “mobile” molecular layers. When thicknesses of the films are three layers and above, the first layers adjacent to mica substrates are strongly adsorbed onto substrates and immobile during sliding; shear is accomplished by the slipping of “mobile” middle layers (results in low friction). For two-layer film (adsorbed layers in direct contact), sliding involves the deformation of adsorbed PDMS segments and wall slip, resulting in high friction. For PDMS films, a “fluid-like” response appears when molecules are squeezed out to final residual thickness (two layers), which is very different from the typical behavior of most of the confined fluid systems (solid-like shift is commonly observed due to confinement). Effects of the substrate-molecule interaction strength and film preparation procedures on the layering structures are also discussed.

SESSION 6

Intermolecular Forces and Interfacial Phenomena affecting Structure and Properties of Thin Liquid Films

Chair: Professor Roger Horn; co-Chair: Professor Dan Schwartz

Previous surface force and nanotribology experiments have raised fascinating questions about the granularity of liquids in thin films; the transition from 3-dimensional to quasi 2-dimensional behavior; surface-induced phase transitions; effects of surface structure and heterogeneity on neighboring liquid; and crossover from continuum to molecular models of structure and dynamics in simple liquids. Similar questions arise in the behavior of complex liquids, including colloidal or nanoparticle dispersions that can be assembled into ordered arrays for novel devices. This session will examine such questions, which will inevitably arise in the fabrication of nanoparticle assemblies for optoelectronic devices, chemical sensors and biosensors, and in microfluidic devices.

Adsorption from Binary Fluids - The Transition from Critical to van der Waals Wetting

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Most experimental and theoretical studies of adsorption from binary fluids have focussed on the critical regime and little work has been done on adsorption in other regions of the phase diagram. In an attempt to correct this imbalance we have used neutron reflectometry to study the composition profile at a solid surface (silicon coated with n-octadecyl chains) in the n-hexane/perfluoro-n-hexane system (critical temperature $T_c = 22.6$ °C, critical mole fraction of n-hexane $\Phi_H = 0.50$). Measurements have been made at temperatures approaching coexistence from above, along three different isochores ($\Phi_H = 0.50, 0.39$ and 0.25) in the one-phase region. This is the “wet” side of the phase diagram, where there is a surface excess of n-hexane. The temperature dependence of the composition profile and the surface excess vary in a complex manner as the system moves away from criticality. The results show that surface effects on the composition profile in a binary fluid become very long range (> 100 nm) as phase coexistence is approached, even at compositions far from the critical. Here, the composition profile decays towards the bulk as z^{-3} , and the surface excess increases as $(T-T_0)^{-1/3}$ as the coexistence temperature T_0 is approached, in agreement with expectations from long-range van der Waals forces.

Film Drainage at Deformable Interfaces – An Exotic Cocktail of Surface Forces and Hydrodynamics

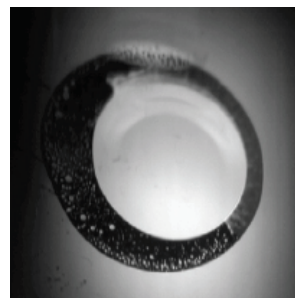
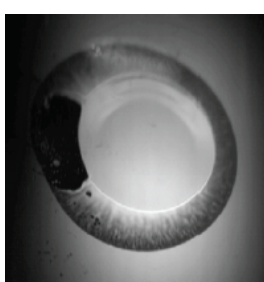
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Film drainage at the interface between immiscible liquids is of both practical and fundamental interest. From a practical viewpoint, both tertiary oil recovery and liquid-liquid separations rely on this phenomenon. Fundamentally, the mixture of hydrodynamics and surface forces in driving film drainage and determining the position of equilibrium makes for an enticing scientific problem. In the past, quantitative study of film drainage at deformable interfaces has been technologically hindered. However recent advances in optical imaging methodologies have provided techniques that can be applied to such systems.

With a view to obtaining quantitative and dynamic data on film drainage at a liquid-liquid interface we have pioneered the application of imaging ellipsometry to such systems, studying the drainage of an aqueous film confined between a solid surface and an oil droplet, as the droplet approaches the surface. Imaging ellipsometry has the advantage that it provides real-time grey-scale optical images of the entire interface as film drainage occurs so that features such as localized film rupture and dendritic spreading can be observed. Cross-sectional analysis of the optical image yields quantitative information on film thickness as a function of time over the entire interface without the need to scan across the surface.



Sequence of grey scale images that show dimpling of the liquid-liquid interface, localised film rupture and spreading dendrites. Note the lifting of the droplet at one end to facilitate film drainage.

We have used imaging ellipsometry to profile the oil-water interface during the drainage of an aqueous film confined between an oil drop and a solid surface. An overview will be presented on the effects of both ionic and non-ionic surfactant on film profiles. The data include features such as dendritic spreading and marangoni stresses and the formation of metastable films. Included will be preliminary data showing how mass transfer across the liquid-liquid interface affects film drainage.

The Role and Measurement of Disjoining Pressure in Lubricant Nanofilms

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The evaporation, wetting and spreading dynamics of polymer lubricants deposited in thin films of thickness $h \sim 1-5\text{nm}$ on plane smooth substrates is governed by the disjoining pressure of the film $\Pi(h)$. When the molecularity of the lubricant manifests itself as oscillations in $\Pi(h)$ the spreading dynamics can be bizarre. In view of the technological importance of the lubricant film in the magnetic recording industry and elsewhere, the measurement of $\Pi(h)$ in this thickness regime as an indicator of film behavior is vital.

An AFM technique has been developed where the disjoining pressure can be measured from the pull-off force between a probe particle on the AFM cantilever and a film covered plane substrate. Results for the fomblin lubricants Z and Zdol on Si surfaces are presented. Experimental difficulties associated with the measurement are discussed.

Using Colloidal Suspensions to Model Atomic Scale Plasticity and Lubrication Phenomena

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Colloidal suspensions have been shown to be excellent model systems for investigating atomic scale phenomena. The advantage of investigating these processes in colloidal suspensions is that we can image the positions and track the motions of the individual particles using fast confocal microscopy. Recently, such suspensions have been used to investigate phenomena ranging from crystal nucleation to gel formation and vitrification. In our lab we have built a shear cell that can be loaded onto a confocal microscope thus allowing us to image the 3-D microstructure of a dense colloidal suspension when it is subjected to an imposed strain.

In this talk I will discuss the progress that we have made towards using colloidal suspensions as model systems for investigating atomic scale lubrication phenomena.

In the course of this talk I will describe a range of striking phenomena that are observed in strained colloidal crystals. I will show that at low strain rates such crystals form dislocations akin to those observed in thin atomic crystalline films.

By studying such defects in colloidal systems we gain access to the detailed dynamics characterizing the defect motion and leading to the ultimate dislocation distribution in the material. At higher strain rates, the viscous stresses induce a different mechanism for stress relaxation. In this regime the crystal layers separate and form sheets that flow over each other. I will then show that even in this regime, when the crystals are sheared in gaps containing less than 10 particle layers they form very different flows from those observed in bulk.

Hydrophobic Interactions at Long and Short Range

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The hydrophobic interaction is among the most important non-specific interactions in biological systems. The significant role of the hydrophobic interaction has led to a great deal of study and yet, over 20 years since the first direct measurement of the long-range attraction between two hydrophobic surfaces, understanding of the origin of this interaction remains elusive. We have measured the attractive long- and short-range hydrophobic forces in water between double-chained surfactant monolayers physisorbed on mica. Effects of dissolved gas on the range of the attraction have been studied, as well. AFM images under water suggest an electrostatic mechanism for the observed long-range attraction, while the origin of the short-range attraction requires further study with a stable system. Preliminary results on a forces between stable octadecyltriethoxysilane monolayers will also be presented.

Bound Water in AOT Reverse Micelles and DPPC Vesicles

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Inverse micelles of AOT/Decane and AOT/Isooctane at low water contents were studied by nuclear magnetic resonance (NMR) and infrared absorption (FT-IR) in function of the water concentration. The molar fraction of bound water was obtained from RMN measurements. Ultrasonic measurements that depend on the compressibility permit to determine the internal radius (water radius) of the micelles. With both results, the size of the bound water layer in this system was found around 0.3 nm. Correlated changes in the FT-IR absorption spectra give us information about the interaction between water and the polar head of AOT. Multilamellar vesicles of phospholipids (DPPC), at different concentrations, have been studied by DSC and FT-IR and present a sub-zero transition near -40°C . This transition is attributed to the interstitial water, i.e. the water confined between two DPPC bilayers. These results emphasize the peculiar properties of the bound water in such systems.

POSTER SESSION

Bridging Nanoscale Forces and Interfacial Phenomena with the Macroscopic World

Chair: Professor Suzanne Giasson

co-Chair: Professor Norma Alcantar

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P1

New Optical Methods In-Situ of the eSFA

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The surface forces apparatus (SFA) is a well-established tool to study the physical properties of confined fluids. Confinement is realized between two atomically smooth mica sheets, silvered on the backside and mounted on two silica supports in a crossed cylinder arrangement. The surface separation is measured locally at the point of closest approach by analysis of the white light interference spectrum transmitted through the thin-film interferometer. For dynamic experiments e.g. squeeze-out of confined fluids or lubrication with molecularly thin films, it is of great interest to image the entire contact area in real-time. We present a novel concept – Optical spectral correlation (OSC) – that uses light transmitted through the thin-film interferometer and analyzes it with a dedicated optical correlator. The correlated light is detected with a CCD camera, yielding a laterally resolved, real-time correlation map. The intensity information can then be readily transformed into physical quantities, such as surface separation and/or local refractive index of the confined film. A simultaneous distance measurement using the conventional Fast Spectral Correlation (FSC) method allows an online calibration of the OSC map. The nominal distance resolution of OSC is limited by the noise of the detected CCD signal, mainly inevitable shot noise. We discuss the requirements of the CCD camera and demonstrate that we can achieve subÅ-resolution in single frame images at sample rates of up to several tens of hertz. In combination with newly developed substrate holders – generating large area contacts with diameters of several hundreds of microns – OSC becomes a powerful tool to study confined fluid films. We present first data showing new aspects of the behavior and the dynamics of such systems.

P2

Adhesion and Stress Relaxation in Living Cells

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Interaction of living cells with a substrate is becoming an important field of research for the scientific community. Cell/surface interactions are known to induce very different responses from cells as apoptosis or active division [1] as well as to affect their rheological properties [2,3]. A precise knowledge of these interactions and their impact on cell behavior is still a challenge because of the variety of their manifestations. We choose to use SFA technique to correlate cell mechanical behavior to their adhesion properties with different model substrates. Living cells were seeded on treated mica surfaces and compression force profiles were performed at 37.2 °C. Mica was functionalized with different self-adsorbed or grafted polymers. Stress relaxation in the cell monolayer was monitored in the decompression force profile by following fringes displacement with time. Data were fitted to several mechanical models in order to extract rheological properties and to compare them with available published data. Preliminary results show a strong dependence of stress relaxation time of the cells with applied force. Influence of substrate will also be discussed.

[1] D.E. Ingber, PNAS 100 (2003) 1472–1474.

[2] N. Desprat, Biophys J 88 (2005) 2224.

[3] M. Puig-de-Morales, E. Millet, B. Fabry, D. Navajas, N. Wang, J.P. Butler, J.J.

Fredberg, Am J Physiol: Cell Physiol 287 (2004) 643.

P3

Hairy and Slippery: Surface Forces and Friction between Surface-Grown Polymer Brushes in Aqueous Media

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Interactions (surface forces and friction) between surfaces at close proximity in aqueous media are important in many technological applications and biological processes. Polymers may be readily anchored on the surface to tailor these interactions, and an effective such strategy is to formulate polymer brushes on the surface. Most often, this is achieved with a “grafting-to” approach, i.e., end adsorbing a polymer to a solid surface. A recent alternative approach is “grafting-from”, i.e., directly growing polymers from a substrate. Using a version of the surface force apparatus, we have measured surface forces and friction between two mica surfaces in aqueous media where such possible different approaches are explored. Our results show that grafting densities of surface-grown polymer brushes attained may indeed be substantially higher than achievable using classical physic-grafting methods. We will discuss the possible implications of our results to the biolubrication process, in which biopolymers end anchored on cell surfaces through trans-membrane proteins facilitate frictionless sliding between biological tissues.

Acknowledgements: I. Dunlop; S. Armes; A. Lewis; & R.K. Thomas.

P4

Interactions and Conformations of DNA and Cationic Surfactants at Hydrophilic and Hydrophobic Surfaces

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Complexes between DNA and cationic surfactants, the so-called lipoplexes, are thought to be useful as potential vectors for gene transfection. Among the factors that control DNA compaction upon interaction with cationic surfactant in the bulk are the nature of both the DNA and the surfactant. In vivo, the complexes will encounter different types of interfaces in the blood stream (walls of protein vessels, blood cells, proteins, etc.) before being thoroughly delivered. Interactions with such interfaces are likely to occur and therefore influence the uptake behavior of the lipoplexes. Hence, the interfacial behavior of lipoplexes will partly determine how efficiently DNA is delivered to the target cells. We have studied the adsorption behavior of DNA and DNA-cationic surfactant complexes on different surfaces by means of ellipsometry and surface force measurements with colloidal probe atomic force microscopy and the surface force apparatus. Results on both hydrophobic and hydrophilic surfaces will be presented making emphasis on the differences of adsorption behavior and interaction with the surfaces of the surfactant-free DNA and the complexes on behalf surfactant type and DNA conformation and length.

P5

Novel Polymer-Metal Nano-Composites for Applications in Detection and Sensing

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Detection of trace elements such as organic contaminants, explosive residues, and metal ions is an intellectually challenging task in science and engineering. It is also a topic of increasing importance due to its impact on the society and the environment. “Stimuli-sensitive” materials are ideal candidates for sensors as they are able to respond to changes in their environment and these responses can be transduced into measurable signals. The purpose of the research in this project is to combine organic polymers with inorganic constituents to tailor the binding properties and the responses of the “composite” material for detection of metals ions in aqueous solutions.

In this project, we focus on a thermally responsive polymer such as poly(N-isopropylacrylamide) (PNIPAM), which exhibits a well-known reversible coil to globule transition in aqueous media with changes in temperature. We are combining cross-linked microgels formed from copolymers of PNIPAM with gold nanoparticles (GNP). By using functional groups in the copolymers as potential sites for binding metal ions and use of imprinting techniques, we aim to explore the composite properties to sense the presence of metal ions in solution. The poster presentation will discuss our experimental approach, results of ongoing work, and future directions.

P6

The Effect of Wettability on Capillary Condensation of Liquid below the Melting Point

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Adsorption and capillary condensation of cyclooctane below its bulk melting point T_m (14 °C) have been studied with a surface force apparatus (SFA). Comparisons were made between bare mica surfaces and fluorocarbon surfaces prepared by adsorbing heptadecafluorodecylpyridinium chloride to mica. As with previously investigated alcohols (*tert*-butanol, *neo*-pentanol, menthol), the capillary condensates remain liquid below the melting point, and their size is inversely proportional to the temperature below T_m . These SFA experiments thus probe melting-point depression in confinement, using a single pore of variable dimension, and the two different surfaces are equivalent to different pore wettabilities. The condensates formed between the fluorocarbon surfaces are smaller those between the mica surfaces. With both surfaces, however, the relationship between the condensate size and the solid-liquid interfacial energy of the condensing substance is different to what was found with the alcohols. The results are discussed in view of the larger contact angle ($\sim 45^\circ$) of liquid cyclooctane on the fluorocarbon surface compared to mica ($< 10^\circ$), and other differences in the wetting behaviour of both solid and liquid cyclooctane on the two surfaces.

P7

Investigating Slip Boundary Conditions with Squeeze Film Measurements in the SFA and AFM

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According to the no-slip boundary condition of hydrodynamics, the flow velocity of a liquid at a solid-liquid interface is equal to the velocity of the solid. The general acceptance of the validity of the no-slip theory for Newtonian liquids is based on experimental observations, rather than on any fundamental theory. In recent years, with the improvement of fine-scale experimental techniques, questions have been raised about the universality of this boundary condition, and whether in some situations the velocity-matching condition should be applied not at the interface but some distance to the solid side of it. This would correspond to the liquid slipping over the solid surface, and the distance between the interface and the (virtual) position of the velocity match defines the ‘slip length’, which is used to characterize the amount of slip. A better understanding of hydrodynamic boundary conditions is important to the study of liquid flow in confined spaces.

The flow of simple liquids in a confined geometry has been studied by means of *squeeze film* experiments, using the surface force apparatus (SFA) and more recently, using the colloid-probe atomic force microscope (AFM). These experiments consist of a thin liquid film confined between two solid surfaces that can be driven up and down relative to one another in a direction normal to both surfaces. In the current project, we investigate and compare the two aforementioned techniques for studying the boundary conditions in the squeeze film geometry, both from an experimental viewpoint and by examining the data analysis and interpretation methods employed. In particular, we present an alternative method of analysis that avoids the subjective judgments required to derive force curves from AFM data (e.g. locating the constant compliance region accurately).

P8

Polymeric Micelles as Soft Colloids: How Far Can We Push the Analogy?

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In water the symmetric triblock copolymer F68, $(\text{PEO})_{76}(\text{PPO})_{29}(\text{PEO})_{76}$ forms spherical micelles upon heating. This intriguing behaviour is used on large scale in industry. But also scientifically this polymeric surfactant is of interest, as the micelles can, under given conditions, crystallize and behave like hard colloidal solutions. Here we report an experimental study of the phase diagram, rheology and dynamics of the symmetric triblock copolymer F68 in water in the presence of sodium chloride. At high temperatures and high polymer concentrations, this system forms a crystal consisting of micelles with an aggregation number of 10-15. The presence of salt qualitatively changes the phase diagram, as it induces a cloud point that is not found in salt-free, aqueous solutions. The appearance of a cloud point inside the 2-phase region is indicative for short ranged attractive interactions between the micelles. This finding is surprising inasmuch as such a liquid-to-liquid phase transition is often obstructed by gelation and thus rarely observed. Above the cloud point the solution becomes unstable and separates into a polymer rich and a polymer poor phase. The aggregation number of the aggregates in the polymer rich phase increases dramatically.

KEYWORDS: Micelles, short-ranged interactions, cloud point, salt effect.

P9

Novel Polymer-Metal Nano-Composites for Applications in Detection and Sensing

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We find that the static structure of charged liposome dispersions, independently of the interaction potential determining it, governs the short-time dynamics in these systems. By light scattering we find evidence of an effective interaction that is not purely repulsive. Existing hydrodynamic models are still able to predict the short-time dynamics of liposomes in suspension when the measured static structure factor is used as input in the calculations. Our results suggest the generality of these theories, which to our knowledge have been only tested in pure repulsive systems.

P10

The Complex Influence of Electrolytes on Bubble Coalescence

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At high concentrations of electrolytes the double layer interaction is screened and short range forces determine colloidal behavior. Consequently the type of ions that are in solution becomes all important and interactions become considerably more complex. In a sense there is a transition from a physics regime (where ions are treated as point charges) to a chemistry regime where the precise character (charge, size, polarisability etc) and pairing of ions is important. Such complexity is exploited universally in nature where it is commonly recognised that ion-specificity is commonplace. It remains a great challenge for colloid scientists to develop a detailed understanding of ion-specificity. Perhaps the simplest system that reveals such complex behavior is that of gas bubbles in salty water.

For one hundred years it has been recognized that electrolytes at sufficiently high concentrations can inhibit bubble coalescence, but an understanding of this phenomenon is lacking. Further, some electrolytes have no influence on bubble coalescence. This complex situation has been described using empirical rules by Craig, Ninham and Pashley in the early 1990's, as set out in the table below. However, an understanding of these rules has not been forthcoming. There have been suggestions that they relate to the influence of ions on surface tension or on gas solubility but the experimental data has not been available to fully test these ideas.

Here we report a considerable volume of work on measurements of surface tension and bubble coalescence of electrolyte solutions, both of single electrolytes and mixed electrolytes performed with the aim of elucidating the nature of specific ion effects in bubble coalescence. This has enabled us to rule out surface tension effects as the mechanism of bubble coalescence inhibition and offers support for a recent suggestion by Marcelja regarding the origin of the combining rules.

Continuation:

Ions		H ⁺	Mg ²⁺	Na ⁺	Ca ²⁺	K ⁺	NH ₄ ⁺	Cs ⁺	Li ⁺	(CH ₃) ₄ N ⁺	(CH ₃) ₃ NH ⁺	(CH ₃) ₂ NH ₂ ⁺	(CH ₃)NH ₃ ⁺
Assignment		β	α	α	α	α	α	α	α	β	β	β	β
OH ⁻	α	×		✓		✓							
Cl ⁻	α	×	✓	✓	✓	✓	✓		✓	×	×	×	×
Br ⁻	α	×		✓		✓		✓					
NO ₃ ⁻	α	×		✓	✓	✓	✓		✓				
ClO ₃ ⁻	β			×									
SO ₄ ²⁻	α	×	✓	✓			✓		✓				
ClO ₄ ⁻	β	✓	×	×			×						
CH ₃ COO ⁻	β	✓	×	×		×	×	×		✓			
(COO) ₂ ²⁻	α	×				✓							
SCN ⁻	β												
IO ₃ ⁻													

✓ Prevents bubble coalescence
 αα= ✓ ββ= ✓
 × No effect on coalescence
 αβ= ×

The effect of different ion pairs on bubble coalescence. αα and ββ combinations inhibit coalescence, whereas αβ and βα combinations have no effect on bubble coalescence relative to pure water behaviour.

P11

Molecular Interactions at the Interface of Nanoemulsions for Drug Detoxification

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Drug toxicity in humans due to illicit drug use, suicide attempts, or iatrogenic complications represents a major health care problem, both in terms of morbidity and economic cost. Many life-threatening drugs do not have specific pharmacological antidotes to reverse the toxic effects that result when an overdose occurs. Therefore, the development of an effective methodology for the removal of free drug from the blood of an overdosed patient in a timely manner (less than 15 minutes) is critically important. In the past few years, efforts have been underway to utilize nanoparticulate systems to accomplish this task. Nanoemulsions are one of the systems that are currently under investigation. Upon injection of a nanoemulsion in the blood of an overdosed person, the nanoemulsion, having extremely high interfacial area, can effectively adsorb drug molecules, and thereby quickly decrease the concentration of free drug molecules in the blood. However, in order to fully grasp their function as toxicity reversal agents, one must understand the molecular mechanism of drug uptake and be able to determine and manipulate the contributing interfacial forces.

Preliminary results from pH studies have led us to believe that electrostatic forces can play a significant role in adsorption/absorption of drug into the nanoemulsion. Amitriptyline Hydrochloride is an antidepressant and as of yet, there is no efficient method to reverse the effects of an overdose in a patient; therefore it is the target drug for the experiments reported here. Amitriptyline has a pKa of approximately 9.4 so that at physiological pH (~ 7.4), it will be positively charged and can thereby interact through electrostatics with a negatively charged nanoemulsion. These nanoemulsions are composed of Pluronic F127, Ethyl Butyrate, and Sodium Caprylate (which gives the negative charge) and are prepared in Phosphate Buffered Saline. The

objective of this study is to develop a better understanding of the important interactions that occur between the microemulsion and the drug.

We have shown, through turbidity analysis experiments, that there is a linear relationship between the Amitriptyline Hydrochloride solubilization capacity of the nanoemulsions and Pluronic surfactant concentration up to a certain Pluronic F127 concentration. Above that critical Pluronic F127 concentration, further titration with Amitriptyline never yields turbidity. We have also seen that turbidity is not observed in systems that do not have sodium caprylate present. Based on these findings we have concluded that at the critical Pluronic concentration, there is no longer any free (unassociated) sodium caprylate molecules in the bulk phase. Therefore, we are able to determine how many molecules of sodium caprylate and amitriptyline are associated with each Pluronic molecule. Each Pluronic F127 molecule can associate with approximately fourteen molecules of sodium caprylate and amitriptyline at the critical concentration (i.e. there appears to be a 1:1 association of sodium caprylate to Amitriptyline). This yields further credence to previous pH studies which showed that electrostatic interactions are important in amitriptyline binding to nanoemulsions produced by Pluronic F127 and fatty acid soap. The findings of this study will provide substantial information regarding the mechanism of reduction of overdosed drugs and will allow us to approximate the uptake capacity of a particular nanoemulsion system.

P12

Study and Evaluation of Adhesion Forces and Chemical Structures Involved in the Aggregation Pathways for Both Amyloid Beta Peptides 40 and 42

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Neuritic plaques in Alzheimer's disease patients are predominantly composed of amyloid beta (A β) peptides with 40 (A β ₄₀) and 42 (A β ₄₂) amino acid residues. We have followed the aggregation pathways for both A β ₄₀ and A β ₄₂ peptides under three different incubation conditions. We have identified three specific conformations of the A β peptides in the aggregation processes. These three conformations are commonly referred as monomeric, oligomeric and fibrillar (1-3) conformations. We have monitored the chemical structures and adsorption behavior as function of time for the peptides dissolved in different incubation media with Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) spectroscopy and Atomic Force Microscopy (AFM). Two principal outcomes were obtained. We have first verified the occurrence of different folding pathways for both A β ₄₀ and A β ₄₂, which revealed that A β ₄₂ peptide is most likely to aggregate as fibrillar conformations and with a higher surface adhesion tendency than A β ₄₀ peptide. And, secondly, we have linked the surface adhesion mechanisms of A β peptides molecules with their secondary structure evolution, which is critical for the formation and stability of monomeric, oligomeric, and fibrillar conformations. The final product of this work will guide us in the searching of ways to destabilize β -sheets secondary structures propitious for the formation of large aggregates such as fibrils that are responsible for the appearance of neuritic plaques in Alzheimer's disease.

P13

Studies on the Monolayer Lubrication and Direct Observation of PFPE Lubricant Molecules by Cryogenic non-contact AFM under Ultra-High Vacuum

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Hard discs are the most important memory media for not only computer systems but also music recording media like i-Pod or for image storage media, etc. Memory density of hard disk systems increases rapidly in recent years and with increasing density, the distance between disc surface and head decreases rapidly. The distance becomes now less than 10 nm and the thickness of the surface lubricant layer is requested to be less than one nm. This thickness corresponds to almost a monomolecular layer or less of lubricant molecules. Almost all hard disk systems use a PFPE lubricant, Z-dol (a commercial name of Solvay Solexis) of which molecules have two OH groups at both ends of PFPE chains. Therefore, this PFPE lubricant can form stable insoluble monolayers at the water surface by spreading from a volatile fluoro-solvent solution, and the surface density of lubricant molecules can be controlled by compression of the monolayer with movable barriers. The monolayer can be transferred to a solid substrate surface by the LB technique. In this paper, we report direct observation of PFPE lubricant molecules by using cryogenic AFM under ultra-high vacuum.

A monolayer of molecular weight fractionated Z-dol (M.W. 1920) is transferred to a surface of gold-sputtered mica, hydrophilic silicon wafer and actual magnetic disk surfaces. Non-contact AFM observation was done using JSPM-4500 at very low temperature under ultra-high vacuum. It was made clear that lowering of the sample temperature to below the glass transition temperature of PFPE is essential to observe PFPE lubricant molecules, and the ultra-high vacuum environment is also essential to prevent freezing of water on the sample at the low temperatures. With increasing sample temperature gradually from 90 K, we could observe molecular images of PFPE lubricant

molecules up to 132 K. At or above 134 K, however, molecular images disappeared. This means that segmental motions of PFPE chains start above this temperature.

Figure 1 shows a non-contact AFM image of Z-dol 1920 lubricant monolayer on the gold-sputtered mica surface. Image size is 100 x 100 nm². Observed particulates are the reversed micelles of Z-dol molecules. On the hydrophilic silicon wafer, we could observe single molecules of Z-dol. On the actual disk surface, however, we also observed the reversed micelles, and they gathered along the ridge structure of the texture of the carbon overcoat of disk surface.

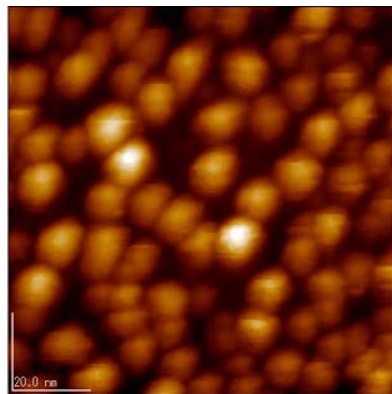


Figure 1, AFM image of Z-dol

P14

Effect of Architecture on the Assembly and Structure of Polymer Brushes

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Polymer brushes are of practical importance because of their ability to straddle phase boundaries and mediate interactions across interfaces. Although a variety of methods exist for tethering polymers to surfaces, one of the most useful methods of creating polymer brushes is via self-assembly of amphiphilic block copolymers. While the structure and properties of linear polymer brushes are well understood, the assembly, structure, and properties of polymer brushes made from branched architectures has not been explored. This presentation will describe our efforts to investigate the impact of chain branching on the self-assembly and structure of polymer brushes made from amphiphilic comb and mikto-arm block copolymers. By monitoring the kinetics of assembly using phase-modulated ellipsometry we find signatures that we attribute to structural reorganizations as the chains become crowded on the surface. Because of increased intramolecular interactions, the equilibrium forces of interaction are also impacted by chain branching. The effect of branching can be incorporated into an Alexander-deGennes type, mean-field model to produce a universal profile that collects the force profiles from brushes of different architecture.

P15

Surface Properties of Charged Polymers Brushes

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Charged polymers at surfaces play a crucial role in designing biomaterials by controlling surface properties and/or functionalizing them. Their role is usually fulfilled by a combination of different types of interaction (electrostatic, steric, hydrophobic, etc). Several experimental and theoretical studies have explored the intrinsic structure and properties of polymer-coated surfaces as a function of grafting density, solvent condition, charge density, ionic strength and pH. The normal and lateral forces between two opposing and moving surfaces bearing different polymers have also been largely investigated. We have shown recently that brushes of charged polymers attached to surfaces rubbing across an aqueous medium exhibit remarkable lubricating properties, even under high compression loads (Nature, 2003, **425**(6954): p. 163-165). However, correlations between molecular conformation of polymer-bearing surfaces and their behaviour are not yet fully understood and are essential for designing biomaterials such as drug delivery systems and wear-resistant implants. To obtain different conformation, we develop a technique to graft different diblocks on surfaces in a control manner.

The approach consists of covalently attaching a thin monolayer of end-functionalized polystyrene (PS) to silica or mica surfaces by adsorption from solution. Then, a PS-b-X diblock copolymer is deposited using the Schaeffer technique (variant of the familiar Langmuir-Blodgett technique). By heating above the T_g and subsequent cooling, the PS blocks of the copolymer diffuse into the end-attached PS monolayer thereby attaching the copolymer onto the surface. We succeeded to build a nice and homogeneous monolayer of PS (with no aggregates and showing no dewetting) on silicon wafers as well as on plasma activated mica surfaces using self-adsorption. AFM revealed wide areas without defects and with a low roughness ($RMS \approx 0.2$ nm). The surfaces initially hydrophilic ($\theta \approx 0^\circ$) became hydrophobic ($\theta \approx 90^\circ$) and the attachment was irreversible confirming the successful grafting of the polymer. On these PS-coated surfaces, we investigated the

behaviour of pH sensitive diblock copolymer, the polystyrene-*b*-polyacrylic acid (PS-*b*-PAA). The presence of the grafted diblock on the PS-coated surface was confirmed by contact angle measurements and AFM. The PS surfaces initially hydrophobic became extremely hydrophilic after grafting. The interactions between copolymers-coated surfaces, measured using Surface Force Apparatus, as a function of different grafting densities and under different environmental conditions such as ionic strength and pH will be presented.

P16

Water in Contact with Hydrophobic Surfaces: Neutron Reflectometry Studies

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Unravelling the interfacial structure of water at hydrophobic surfaces embodies potential answers to the experimentally observed finite-ranged attractive forces between hydrophobic surfaces in water and the reduced drag on water flowing in hydrophobic channels. These ‘hydrophobic interactions’ are involved in diverse phenomena including protein folding, amphiphile self-assembly, membrane fusion and ‘super-hydrophobicity’. The range and origin of this interaction has remained unresolved for 20 yrs. Here, direct non-invasive neutron reflectivity measurements reveal the presence of a reduced (deuterated) water density region, with a sigmoidal density profile at the hydrophobic silane-water interface that depends on the type and concentration of dissolved gases in the water. Removal of dissolved gases decreases the width of the reduced water density region, and their reintroduction leads to its increase. When compared with recent computer simulations a locally fluctuating density profile is proposed, while pre-existing nano-bubbles are excluded. The presence of a fluctuating reduced water density region between two hydrophobic surfaces and the attractive ‘depletion force’ it leads to, may explain the hydrophobic force, its reported diminution in deaerated water, and the near slip boundary condition for water flowing in hydrophobic channels.

P17

Phase Transition Behavior, Morphological Changes, and Lipid Interactions in Myelin Sheath

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Myelin is a stacked membrane structure that allows for fast, efficient conduction of nerve impulses. It has 8 kinds of lipid molecules on two alternating bilayers and proteins such as Myelin Basic Protein (MBP) which has an important role in maintaining myelin structure. The compact bilayer organization of healthy myelin is believed to require a well-defined range of lipid and protein composition, and bilayer-bilayer interaction. Even though we know that multiple sclerosis (MS) is a morphological transformation involving loss of adhesion between myelin lamellae and sometimes formation of myelin vesicle, its mechanism and causes for demyelination is still under investigation. We have used fluorescence microscopy, Langmuir isotherm, and Langmuir-Blodgett techniques to investigate how lipid composition of myelin lipid system affects the phase transition behaviors of myelin monolayers and bilayers depending on lateral pressure, temperature, and pH conditions. We currently study the topographic changes and the interactions of two symmetrical myelin bilayers in the absence and presence of MBP isoforms using Atomic Force Microscopy (AFM), and Surface Force Apparatus (SFA) techniques. The acute experimental allergic encephalomyelitis (EAE) in the common marmoset which is a highly relevant model of MS was used as a comparison.

P18

Ionization and Molecular Recognition Phenomena in Self-Assembled Surfaces of Bowl-Shaped Macrocyclic Molecules

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The goal of this project is to understand the ionization of self-assembled surfaces of macrocyclic molecules. These molecules act as hosts for recognition of charged guest species. Specifically, self-assembled monolayers (SAMs) of tetrathiol and tetrasulfide derivatives of calix[4]resorcinarene on gold substrates were prepared. Ionization of these SAMs was investigated using a surface plasmon resonance (SPR) technique and contact angle measurements. Solutions of varying pH were used as a probe to test the differences in the advancing angles on these SAMs. As the pH of the solution increases and the surfaces undergo ionization, the change in the balance of interfacial energies is reflected in the contact angle measurements. SPR characterization allows measurement of the optical thickness of ultra-thin films and to monitor the dielectric changes at a solid-liquid interface in a non-invasive and real-time manner. For surfaces of both resorcinarene derivatives, contact angles decrease as the pH of the probe liquid increases and SPR measurements show that dielectric changes in the surface occur with increase in alkalinity. The results of SPR measurements, contact angle changes and a model for fitting the optical data from SPR will be presented to provide a fundamental understanding of the ionization in the self-assembled surfaces.

P19

Micropatterning of Proteins: a New Approach Using Dewetting Principles

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The ability to control protein and cell positioning on a microscopic scale is crucial in many biomedical and bioengineering applications, such as tissue engineering and development of biosensors. We propose here a novel micro-patterning technique that does not require templates, molds or stencils and is based on patterning polymer films bilayers by dewetting processes, followed by the selective adsorption of proteins from buffer solutions. Evidence is obtained by fluorescence microscopy and atomic force microscopy (AFM) that proteins adsorb preferentially on isolated bio-adhesive micro-patches in a protein-resistant background. The surface density of proteins inside the adhesive islands can be tailored by varying the concentration of the protein solutions employed. Furthermore, the method can also easily produce inverse patterns, containing non-fouling islands in a protein-adhesive matrix. The produced micropatterned substrates should prove useful to studies in biosensor and bioassay development and as substrates to study growth and motility in cell cultures.

P20

Peptide-Modified Responsive Surfaces with Built-in Logic

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The overall thrust of our research program is to develop well-behaved responsive surfaces without the need for complex circuitry or bulky instrumentation. Our approach is to use surface-attached, cross-linked polymer films that can be toggled from a collapsed to a swollen state or vice-versa in response to an external stimulus, which could be temperature, pH, or a small analyte. The stimulus alters the balance of hydration forces in the responsive layer, resulting in changes to the swelling of the layer. We aim to build logic directly into the layer structure via embedded peptides that can modify the balance between hydrophobic/hydrophilic interactions depending on the conformation of the peptide.

Poly-N-isopropylacrylamide (Poly-NIPAAm) is a well-known and studied thermoresponsive polymer. We demonstrate that the transition temperature of poly-NIPAAm networks can be precisely controlled with small peptide sequences. Starting with a poly-NIPAAm network copolymerized with a lysine like monomer, N-(3-aminopropyl)methacrylamide hydrochloride, we show that we can synthesize peptides directly into the Poly-NIPAAm network using standard Merrifield Solid Phase Peptide Synthesis techniques. Ultimately, this strategy will allow ability to formulate peptide embedded Poly-NIPAAm networks with programmable response characteristics.

P21

Long-Range Attraction between Charge-Mosaic Surfaces

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Surfaces with heterogeneous charge density are ubiquitous in biological systems, and it has recently begun to become clear that this non-uniformity of surface charge is crucial in determining their function. In this work we present experimental measurements of the interactions between model surfaces decorated with a mosaic of positive and negative charge patches. The nature of the surface is revealed by AFM and contact angle studies, and the interactions between them, across pure water and aqueous salt solutions, are measured using a Surface Force Balance [1]. We reveal a long ranged attraction between the charge-patched surfaces, and relate these findings to theoretical predictions and models [2, 3]. It appears that the length scale of the interaction is determined by either the patch size or the Debye length, whichever is the shorter.

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P22

Molecular Transport Facilitated Using Corona Charge as a Novel Non-Contact Means

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We have shown here for the first time that application of Corona charge produced in air, to B16 murine melanoma cells in-vitro results in molecular delivery across the cell membrane. Among the many methods of corona discharge one of the methods to generate corona ions is by breaking down of air at room temperature, by the application of a high voltage. The interaction of these charged particles with biological cells was studied and their possible use for molecular delivery was investigated. There is no known work in the literature at this time using this kind of non-contact technique for molecular delivery. Molecular delivery was tested with SYTOX-green nucleic acid stain that is not permeable to cells with intact cell membranes. It was found that there was a significant increase in the amount of SYTOX ($P = 0.003$; statistical significance is assumed for $P \leq 0.05$) delivered to the cells exposed with the corona charge. The results of this study demonstrate that corona discharge can be safely used as a novel means of non-contact molecular delivery. The use of this method will be explored for delivery of drugs and genes to cells in-vitro and animals in the near future.

P23

Society of Women Engineers

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As a member of the chemical engineering community, I have a keen interest in the international thoughts and knowledge in the world of surface materials and their interactions. Through my cooperative education employment with Mosaic Company, the world's largest fertilizer company, I have been introduced to the importance of surface interaction in the manufacturing field. Too many times the interactions on the smallest level are forgotten when looking at such a large picture. Yet, when it comes to chemical reactions, if we do not take into account those interactions, we are remiss in thinking that we understand the fundamental basics of our model. I personally have a responsibility as a student at the peak of my education to seek out resources such as the SFA Conference 2006 to increase my knowledge in my future field.

As President of the University of South Florida section of Society of Women Engineers, I also have an overwhelming responsibility to become more involved in the field of engineering, especially when interacting in the international community. Bringing together world renowned minds is also bringing together a room of persons who can touch the world and our children, helping each young person to possibly decide in a future in engineering. Society of Women Engineers promotes not only getting those young children the information they need to become engineers, but encouraging the women in the engineering world to become more educationally involved in their fields. It is only through international understanding of the lack of female interactions in the engineering field that we will one day have a more balanced field that couples the strengths of both genders.

My hope is that SFA Conference 2006 will offer me the opportunity to learn with the international community. After all, it is only through knowledge that we will ever make a difference.

P24

A Model with Microstates for Rheological Modelling of Complex Fluids

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In this model, the dynamics of a transient network are analyzed by two coupled kinetic processes which describe the rheological behavior of complex fluids. Five microstates are defined, representing the complexity of interactions among the macromolecules suspended in a Newtonian fluid. These microstates represent statistical networks with varying entanglement density, such as a dense entangled network in one extreme, and free chains or dangling ends (pendant chains) on the other extreme. It is assumed that the energy barrier required to modify the complexity of the system can be provided by the flow, and that the flow-induced change in the network complexity is modeled as a coupled kinetic scheme constituted by a set of reversible kinetic equations describing the time evolution of the microstates. The model predicts shear-banding in steady simple shear and time-dependent non-linear rheological phenomena, such as thixotropy.

P25

Viscoelasticity and Surface Forces in Systems with Alkyl Polyglycoside Surfactants

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The adsorption behavior of non-ionic glycoside, sugar surfactants at the air/liquid and solid/liquid interfaces were studied by using surface laser light scattering (SLS), surface forces and thin film pressure balance (TFPB) techniques. The viscoelastic properties (surface elasticity and surface viscosity) of monolayers formed by isomers of octyl glucoside and 2-ethylhexyl glucoside surfactants were quantified at sub-micellar concentrations and it is shown that diffusional relaxation model describes the observed trends in high-frequency, non-intrusive SLS. The interfacial diffusion coefficients that resulted from fitting this diffusional relaxation model to surface elasticity values obtained with SLS reflect the molecular dynamics of the subphase near the interface. The long-range and adhesive forces acting between non-polar surfaces coated with sugar surfactants were also measured with a bimorph surface force apparatus. After consideration of hydrodynamic interactions the results were compared with disjoining pressure versus thickness curves that were obtained with the thin film pressure balance. It was observed that the stability of thin liquid films crucially depends on the surfactant's bulk concentration (c) and thus on the packing density and viscoelasticity of the adsorbed layer. The force barrier preventing removal of the surfactant layer from between two solid-liquid interfaces increases with increasing c , while for foam films it is the stability of the Newton black film that increases with c .

P26

Microemulsions as Drug Delivery System: Propofol Microemulsions for Anesthesia

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Microemulsions are excellent candidates as potential drug delivery systems because of their improved drug solubilization, long shelf-life, and ease of preparation and administration. Depending on the type of drug, all three types of microemulsions (i.e. oil-external, water-external and middle-phase microemulsion) can be used for drug delivery. In the present study, Propofol (2,6-diisopropyl-phenol) was selected as a test drug to form water external microemulsion.

Propofol is intravenous general anesthetic drug, having several favorable anesthetic characteristics, including rapid emergence from unconsciousness without drowsiness. Propofol is water insoluble and currently used in a macroemulsion form, which has various side effects. In the present study, several oil-in-water microemulsions constituting Propofol (oil), biodegradable non-ionic Pluronic polymers, and ionic fatty acid salts were formulated. Various properties of these microemulsions, like particle size, stability on dilution, and pH etc. were measured as a function of time, which shows that these systems are stable.

Anesthetic studies of these stable microemulsion systems were done using randomized crossover design in rats. Rats randomly received propofol (10 mg/kg/min) either as a microemulsion or conventional macroemulsion (Diprivan®) to determine these endpoints: induction (dose; stunned; loss of lash reflex, righting reflex, withdrawal to toe pinch) and recovery (recovery of lash, righting, withdrawal reflexes). After 14 days, rats were crossed over into the opposite limb of the experiment. All rats experienced anesthesia with successful recovery although significantly greater doses of propofol were required to induce anesthesia with microemulsions irrespective of surfactant concentration or type.

Propofol microemulsions caused general anesthesia in rat similar to that resulting from macroemulsions. The surfactant concentration and type markedly affects the spontaneous destabilization and anesthetic properties of microemulsions, a phenomenon suggesting an approach whereby pharmacodynamic properties can be selectively modified.

P27

Application of Mesogens to New Write-Once Media for Polarization Holograms

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Holographic storage media such as azopolymers, which can record not only intensity-modulated gratings but also polarization-modulated gratings, have been expected for high signal-to-noise ratio (SNR) recordings in the digital data storage. Acting as a wave plate, the polarization gratings can be used to isolate a data signal from the output. The polarization-recordable media, however, cannot fix the polarization modulation because they realign by the following irradiation. We investigated the complex of the azopolymer and photocurable liquid crystals as new hologram media. When the polarized light induced the alignment of the azopolymer, the photocurable liquid crystals oriented as well as the azopolymer by the interaction between the mesogens. Then the only photocurable liquid crystals cured to become polymers and fixed their orientation. This liquid crystal polymer could keep the orientation even after the differently polarized irradiation, while the azopolymer changed the orientation. As a result, we have successfully demonstrated that the proposed complex can act as write-once-read-many polarization-recordable media. Additionally, we obtained the sensitivity of the complex 10 times larger than that of the simple rewritable azopolymer. This effect also depends on the interaction between the mesogens. The sensitivity of the complex kept a certain value even after a serial exposure for multiplexing, while those of well-known photopolymers decreased dramatically. This is because the complex contains the azopolymer that can change the orientation by overcoming the mesogen interaction with the irradiation. The volume multiplexing in holographic data storage requires the constant sensitivity. Therefore, the proposed media, which is polarization-recordable, write-once-read-many and high sensitive, is very promising and practical for digital holographic storage.

P28

Adhesion and Friction of Polystyrene Surfaces: Temperature Effects

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Using a Surface Forces Apparatus (SFA) we have studied the adhesion and friction of polystyrene (PS) thin films on mica having various molecular weights from 580 Da ($T_g = -45$ °C) to 1,300 Da ($T_g = +39$ °C). The temperature was varied from 23 to 65 °C, thereby spanning the T_g of the polymers, and the film thicknesses of 30–90 nm were much greater than the radii of gyration ($R_g \approx 1$ nm) of these polymers. Particular attention was given to rate- and time-dependent effects on the adhesion and friction forces. At $T > T_g$ the polymers behave like liquids, and at low detachment and shearing rates their adhesion and friction forces are accounted by their surface energy and bulk viscosity, although fingering instabilities and cavitation accompany the detachment. For the higher MW polymers (PS 1240 and PS 1300) at temperatures below or near T_g , the adhesion and friction forces increasingly depend on the density of chain ends at the surfaces. The adhesion hysteresis peaked close to the bulk T_g , but also depended on the load, contact time, and detachment rate. Certain correlations and scaling relations were obtained, such as the adhesion force *versus* separation rate V_{\perp} , which was found to vary as V_{\perp}^n where $n \approx 0.15-0.36$ depending on the experimental conditions. We discuss these findings in terms of the bulk and surface molecular properties of interacting polymer surfaces above and below T_g .

Activities

Chichen Itza



Sunday, May 7 (7 AM - 6 PM). You will enjoy an interesting drive into the heart of the Yucatan Peninsula. Chichen–Itzá is one of the world’s most important archeological sites. Founded over a thousand years ago by the Mayans, it was soon abandoned by them and restored by the Toltecs in the 12th century, who made it the capital of their powerful empire. You can explore the wonders of the city, including the CASTLE OF KUKULCAN with its pyramid which stands almost 150 feet tall. In the recesses of the castle is one of the treasures of North America, a red painted jaguar, set with 73 pieces of jade. There is also a 60-foot deep sacred well, where jeweled virgins were once sacrificed to the rain god, Chac. Also visit the OBSERVATORY where the Mayans observed the movements of the heavens and developed their remarkable calendar. This is a full day tour, recommended for those who are enthusiastic about ancient cultures and history. Once at the site, it is a complete walking tour so bring your comfortable walking shoes.

Tulum



Wednesday, May 10 (12:30 PM - 5 PM). Imagine yourself in the midst of the ceremonial and trading center of the great Mayan civilization. This tour gives you a glimpse into that magnificent society with a visit to the ruins at Tulum, which date back to 1200 A.D. Perched atop a high cliff overlooking the Caribbean Sea, Tulum was the first of the Mayan structures to be spotted by Spanish explorers in the 16th century. Tulum's most prominent structure, EL CASTILLO, is located on a 40-foot bluff and at one time functioned as a lighthouse to help guide ships through the treacherous reef that lies off shore. Another interesting structure is the TEMPLE OF THE FRESCOES, with its friezes which still have the original pigment used to stain the carved figures. Following the guided tour of the archeological zone, you'll have time to wander around on your own. After walking among the ruins left by some of México's earliest habitants, your tour may continue on to Xel-Ha. Xel-Ha is one of nature's perfect creations and a paradise for nature lovers. Xel-ha means "where waters are born". This unique place is formed by a combination of inlets, lagoons, cenotes (sinkholes) and caves that are fed by the sea and underground fresh water springs and rivers, turning Xel-Ha into the world's largest natural aquarium. Surrounding this enormous body of water is a wild jungle that can be explored on foot. Come and enjoy this special place and spend your day snorkeling, enjoying the beach, swimming with dolphins (at additional cost) or just relaxing in the jungle's shade.

Jungle Tour Snorkel Adventure



Monday (TBA). A world filled with exotic tropical birds, plants and marine life awaits your exploration. While driving your own Aqua Ray vehicle (similar to a wave runner, two passengers per vehicle) / Speed boat, experienced guides will lead you on an exciting tour through the dense lagoon mangroves, to the turquoise waters of the Caribbean. There you can relax and snorkel at Punta Nizuc, the largest

Maps

Hotel and Convention Center Location

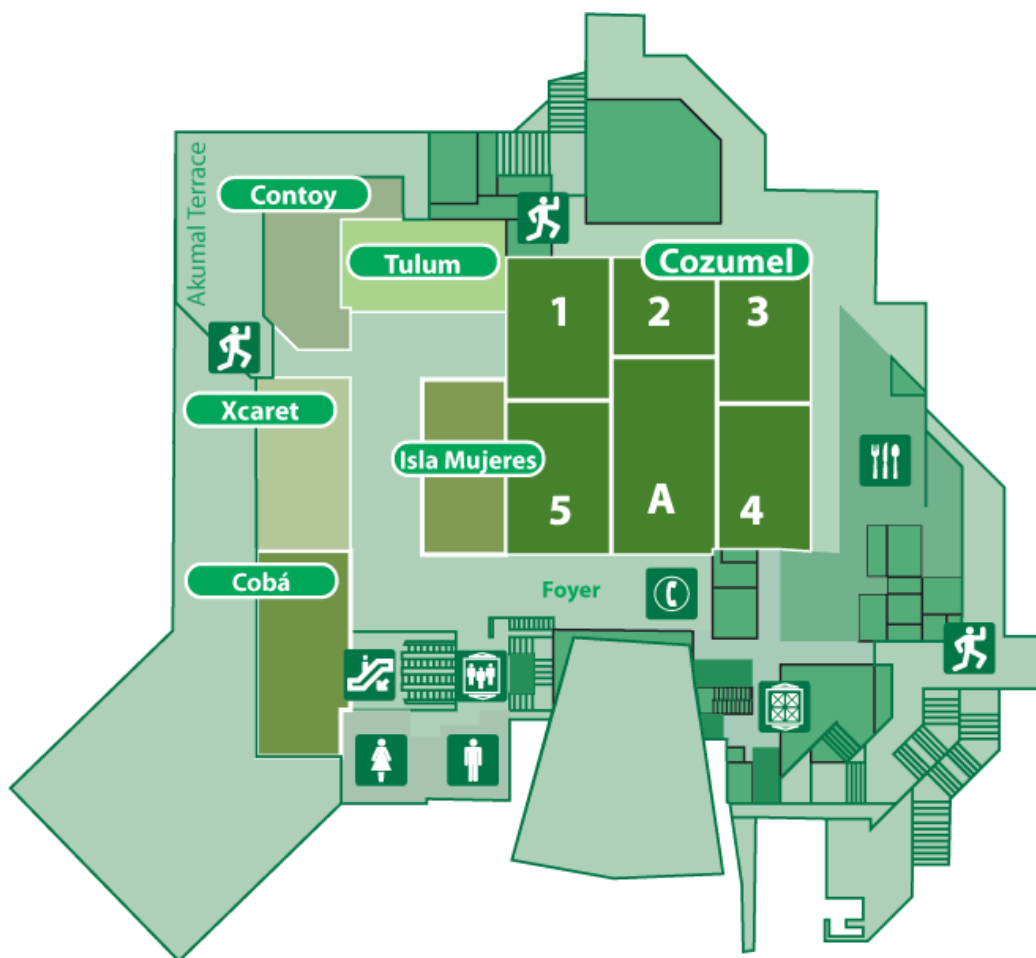


All talks will be held in the Cozumel Room

Cancun Center, Conventions & Exhibitions
Boulevard Kukulcan KM. 9, Level 2
Zona Hotelera 77500 Cancún, Q. Roo, México



LEVEL 2



Map of Cancun Region

Hotel Presidente
InterContinental



www.mapgraphics.com

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